LXXII. *Relations between Young's Modulus and other Physical Quantities.* By JAS. P. ANDREWS, *B.Sc., East London College* [*].

THE work of Clemens Schaefer in 1900 and 1902 [†], on the elasticity of pure annealed metals at low temperatures, and the more recent determinations of Young's Modulus at high temperatures by Dodge [‡], Harrison [§], Koch and Die-terle [‖], and the writer [¶], have provided us with a fairly complete account of this quantity for a number of metals throughout the range −186° C. to near the melting-point. In the light of this fact, the various attempts which have been made during the last century to connect Young's Modulus with other physical constants may be profitably reconsidered with the object of increasing the usefulness of such relations, and of throwing some light on the cause of the variation found.

One of the best known relations is that between the modulus and the atomic volume. Thus Wertheim[**], in 1844, gave a list of numbers to show that $q V^{7/3}$ was constant (at

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[*] Communicated by the Author.

[†] C. Schaefer, *D. Phys. Gesell. Ver.* ii. p. 122 (1900); *Ann. d. Phys.* v. p. 230 (1901); *Ann. d. Phys.* 1902, p. 670.

[‡] H. L. Dodge, Phys. Rev. xi. p. 311 (1918).

[§] E. P. Harrison, Proc. Phys. Soc. Lond. xxvii. p. 8 (1914).

[‖] K. R. Koch and R. Dieterle, *Ann. d. Phys.* lxviii. 5. p. 441 (Aug. 31, 1922).

[¶] Lees, Shave, and Andrews, Proc. Phys. Soc. Lond. xxxvi. p. 405 (1924), and J. P. Andrews, Proc. Phys. Soc. xxxvii. p. 169 (1925).

[**] Wertheim, *Ann. de Chimie*, Tome xii. (1844).

any rate approximately), where V was the atomic volume, and q Young's Modulus. The formula was based on his own observations at ordinary temperatures, but was verified later (again approximately) by Tomlinson [*]. In 1892, Fessenden [†], in an attempt to explain the interatomic attractions by the electrostatic law of inverse squares, calculated (to a rough approximation) that qV^2 should be the same constant for all metals, and made the interesting remark that, owing to temperature variation, q should be measured at the same fraction of the melting-point for all metals. Peczalski [‡] arrived at the same law on much more general grounds in 1922, although the ideal structure he assumes for a metal, viz., a regular arrangement of atoms on a cubic space-lattice, combined with complete isotropy, could be expected to correspond neither with the assemblage of æolotropic crystals in actual samples of metal, or to single crystals of the metals. In view of this, and of the further fact that the argument seems to me to lead to the law $qV^2 =$ const. as given by Wertheim, it is not considered worth while to enter into the detail of this hypothesis. The second power law is found to be a bad approximation for metals of high melting-point, and Portevin [§] for this reason considers that empirical relations of the type $qV^b = kT^a$, where T is the absolute temperature of fusion, a is nearly 1, and b nearly 2, are better. An empirical relation bearing some resemblance to these was proposed by Sieglerschmidt [‖] in 1911, the formula, viz. $\dfrac{q}{s} = 34000 \left(\dfrac{1}{A\alpha}\right)^{1\cdot2}$, where s is the specific gravity, A the atomic weight, α the coefficient of linear expansion, reducing to $qV^{1\cdot2} s^2 a^{1\cdot2} = 34000$ in virtue of the relation $A = Vs$.

At the conclusion of his work at low temperatures already mentioned, and among several important generalizations, C. Schaefer drew attention to a relation between the temperature coefficients of elasticity, the atomic volumes, the coefficients of expansion, and the melting-points of the elements. He defined the relation no further than by showing a regular curve between the temperature coefficient of rigidity and the absolute melting-point, with the implication that a similar curve could be drawn for Young's Modulus.

[*] H. Tomlinson, Phil. Trans. p. 32 (1883).
[†] R. A. Fessenden, Chem. News, lxvi. p. 207 (1892).
[‡] T. Peczalski, *Comptes Randus*, clxxvi. p. 500 (1923).
[§] A. Portevin, *Comptes Rendus*, 8 Oct. 1923, p 635.
[‖] H. Sieglerschmidt. *Ann. d. Phys.* xxxv. p. 775 (1911).

Some theories of the solid state are capable of yielding an expression for the temperature variation of Young's Modulus. But the present tests cannot in general be applied to these, for they require a knowledge of the temperature variation of Poisson's Ratio which we do not possess. An example is afforded by Grüneisen's [*] theory, which, although it cannot for this reason be used here, is mentioned because of a definite attempt by Ratnowsky [†] in 1913 to make the theory account for temperature variations in elasticity in a more precise way.

Grüneisen's theory was based on the principles of classical physics : Ratnowsky applied to it the quantum theory, employing the method that Debye [‡] used to explain the variation of specific heats at low temperature. In this theory, the ratio of the absolute temperature to a certain "Critical" or "Characteristic" temperature is called the "corresponding temperature" of the substance, and Ratnowsky found that $\dfrac{V\beta}{k_T}$ should be the same function of the corresponding temperature for all substances, where k_T is the isothermal compressibility, V the atomic volume, and β the coefficient of cubical expansion. This relation might have been put to the test but for a logical difficulty [§].

One other example is afforded by Sutherland's equation [||]

$$q = q_0 \left(1 - \cdot 823 \, \frac{\theta}{T} \right),$$

where q_0 is the value of Young's Modulus at absolute zero, θ the absolute temperature, T the absolute melting-point, which was obtained empirically "with singular ease" with very inferior apparatus.

[*] E. Grüneisen, *Ann. d. Phys.* xxxix. p. 257 (1912).

[†] S. Ratnowsky, *Deutsch. Phys. Gesell. Verh.* xv. p. 74 (1913).

[‡] P. Debye, *Ann. d. Phys.* xxxix. p. 817 (1912).

[§] For the argument upon which this is based is fundamentally unsound, a hypothetically constant compressibility being employed to calculate the critical temperature, and this in turn to calculate the variation of compressibility. Up to about halfway to the melting-point, however, the elastic constants do vary slowly, and in this range the proposition may be an approximation. The matter may be summed up with the remark that an investigation of the relation showed that the metals are separated into unexpected groups such as Fe, Ni, Zn ; Ag, Sn ; Au, Pt, Pb ; to each of which the relation applies, separately, as an approximation which extends up to half the absolute temperature of fusion. It will be noted that metals in the same row of the periodic table are grouped together, not those of the same column as might have been anticipated.

[||] W. Sutherland, *Phil. Mag.* xxxii. pp. 32, 215, 529 (1891).

A much more promising formula is that given by Lejeune [*], and according to which q, Young's Modulus, is equal to ten times the total quantity of heat Q required to raise 1 c.c. of the metal to the melting-point and then convert it into liquid, *i. e.*,

$$q = 10Q \quad (q \text{ measured in kg/mm.}^2).$$

General Remarks.

An inspection of the curves shown in fig. 1 shows that for each metal the variation of Young's Modulus with temperature takes place in two stages, viz., a slow decrease

Fig. 1.
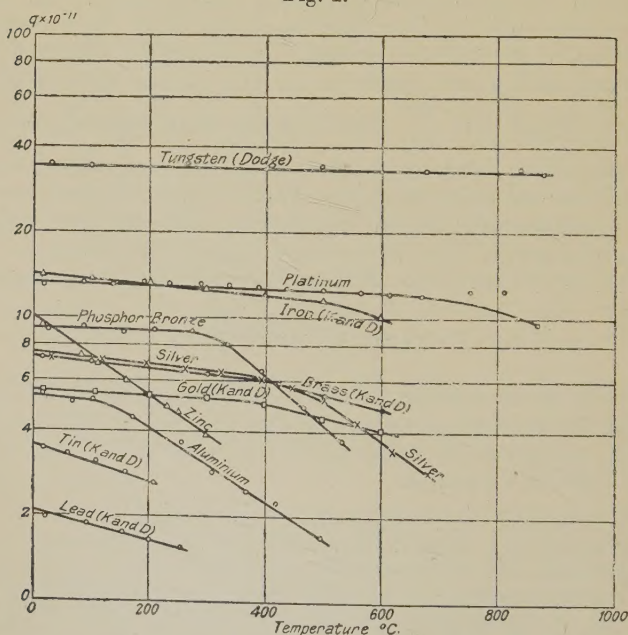
at low, and a rapid decrease at high temperatures, the change taking place at approximately half the absolute temperature of fusion.

It has been shown [†] that the curves may be described by formulæ of the type $q = q_0 e^{-bt}$, but that for each curve the constants q_0 and b_0 are different for the two parts. The

[*] F. Lejeune, *Sitz. Wien. Akad.*, 122, xi. *a.* p. 739 (1913).
[†] J. P. Andrews, *loc. cit.*

distinction to be drawn between these two sections of the curves is emphasized by the fact that viscous flow in the metals begins about halfway to the melting-point, with the consequence, first, that Young's Modulus becomes much more difficult to measure, and second that the proportionality between stress and strain becomes doubtful, during the more rapid decrease. Now it happens that metals of low melting-point exhibit the rapid decrease at ordinary temperatures, while those of high melting-point are in the slowly decreasing stage ; yet each of the above relations rests on values of q measured near $0°$ C. only. It is proposed in the following tests to use values of q measured at the same fraction ϕ of the absolute melting-point, as Fessenden probably meant. Two cases will be anticipated for each of the relations tested, corresponding to each part of the curves, and of these the second should be accepted with considerably more reserve than the first. The actual experimental curves have been employed.

The Atomic Volume Relations.

The simplest form of this relation is of the form, $qV^x =$ constant, where x is a constant. Assuming the form to be correct for values of q chosen at the same fraction ϕ of the absolute temperature of fusion, we proceed to find the values of the constants by plotting $\log q$ (selected at one value of ϕ) against $\log V$, and drawing the nearest straight line through the points.

The scatter of the points is wide enough to allow doubts as to the validity of the relation [*], as fig. 2 below shows, but considering the relation to be allowable, the following table shows the value of the constants deduced.

Fraction of absolute melting-point, ϕ.	·20	·25	·30	·35	·40	·50	·55	·69	·65	·70
x	2·4	2·3	2·3	2·3	2·3	2·1	1·7	1·7	1·6	1·4
Constant $\times 10^{-13}$	15·5	14·4	12·9	12·3	11·5	7·6	3·0	2·4	1·6	·95

[*] This wide scattering is probably due to the results having been obtained by different observers, on different specimens, whose purity and previous treatment differed considerably.

Up to ·50 of the melting-point, we have $qV^{2\cdot3}=k$, and above ·55 of the melting-point, $qV^{1\cdot6}=K$, where k and K are
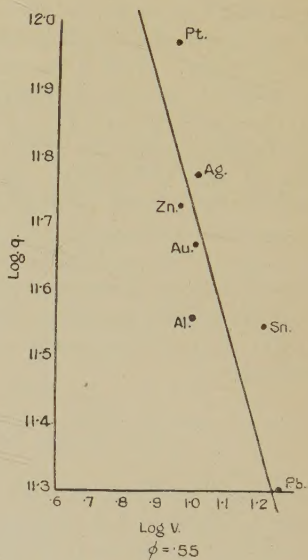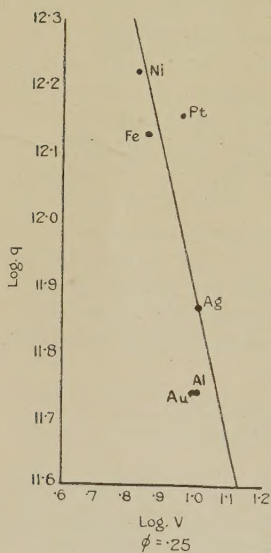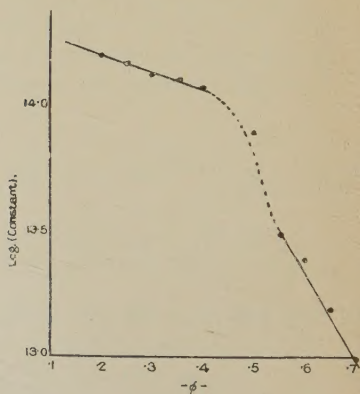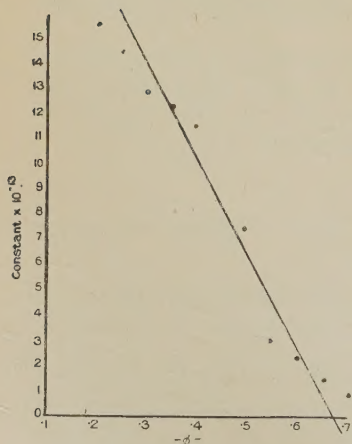
Fig. 2.

Fig. 3.

functions of ϕ. An idea of the form of the functions may be obtained by plotting the constant or its logarithm against ϕ as in fig. 3.

From the first graph it is clearly possible to express the connexion by two linear functions of short range, or less accurately by one linear relation as shown. Either of these alternatives gives the nearest approach to Portevin's linear relation, but they do not accord with experiment so well as the linear parts of the logarithmic curve *. These give the equations

$$\log_{10} k = 14\cdot34 - \cdot72\phi \text{ for lower temperatures, and}$$

$$\log_{10} K = 15\cdot4 - 3\cdot43\phi \text{ for high temperatures.}$$

This method leads us rather far from the observations, and assuming the form to be given by the functions above, it is better to estimate the constants directly from the observations. This was done for the former of these equations, and led to the improved relation :—

$$\log_{10} k = 14\cdot44 - \cdot90.$$

The following list shows the extent to which the relation, which may be written in full as

$$q\mathrm{V}^{2\cdot3} = (2\cdot75 \times 10^{14}) \times 10^{-\cdot90\phi} \quad \text{up to } \phi = \cdot5$$

and $\quad q\mathrm{V}^{1\cdot6} = (2\cdot51 \times 10^{15}) \times 10^{-3\cdot43\phi}$ for $\phi > \cdot55$,

may be used to predict q at 0° C. The column of observed

Substance.	$\mathrm{V}^{2\cdot31}$.	$\mathrm{V}^{1\cdot61}$.	Melting-point	q calc. $\times 10^{-11}$.	q obs. $\times 10^{-11}$.
Aluminium	205	—	930 abs.	7·15	6·2 – 7·3
Gold	214	—	1330	8·38	6·9 – 9·3
Iron.........	91·6	—	1800	21·9	19·6 –21·6
Platinum...	164	—	2030	12·7	15·7 –17·2
Silver	218	—	1235	7·98	5·9 – 7·8
* Copper ...	92·9	—	1357	19·4	10·2 –13·0
* Nickel	80·6	—	1720	24·0	19·6 –21·6
* Palladium	171	—	1820	11·8	9·8 –14·0
* Bismuth ...	—	132	542	3·55	3·15
* Cadmium	—	65·1	594	10·3	4·9 – 6·9
Lead	—	105	600	6·67	1·47– 1·67
Tin	—	87	505	4·04	3·9 – 5·4

* For the linear law $q\mathrm{V}^x = a\phi + e$ would not reduce to the form $q = q_0 e^{-bt}$, for a single metal, as experiment shows it should, whereas the logarithmic form will.

data is compiled from Landolt-Börnstein's tables, and not from the curves already used, because the calculation of the law involved a broad averaging, and we should not expect minute agreement with these individual observations. Substances marked with an asterisk were not used in the previous work.

Particular cases.

(1) At any particular value of ϕ, and for metals at temperatures less than half their melting-points, $qV^{2\cdot3} = \text{constant}$, which is strikingly like Wertheim's rule $qV^{7/3} = \text{constant}$.

(2) At low temperatures, ϕ is small, and the relation may be expressed as $q = q_0(1 - b\phi)$, which reduces to the form Sutherland proposed.

Other Allied Relations.

(1) *Sieglerschmidt's Relation.*

This may be written as $qV^{1\cdot2}s^2\alpha^{1\cdot2} = 34000$, where α is the coefficient of linear expansion. Now it is already well known that the coefficients of expansion are functions of the atomic volumes, the following list showing a number of substances which follow the simple law $\alpha = 8\cdot11 \times 10^{-7} \times V^{1\cdot35}$ fairly well. It includes most of the substances from which Sieglerschmidt obtained his expression.

Substance.	α calc.	α obs.	Substance.	α calc.	α obs.
Al	$16\cdot2 \times 10^{-6}$	$22\cdot2 \times 10^{-6}$	Pb......	$40\cdot4 \times 10^{-6}$	$29\cdot3 \times 10^{-6}$
Cd......	$27\cdot4$	$29\cdot7$	Mg ...	$26\cdot8$	$26\cdot1$
Co	$10\cdot6$	12 (approx.)	Ni	$11\cdot1$	$13\cdot0$
Cu......	$11\cdot4$	14 (approx.)	Pt	$15\cdot9$	$8\cdot85$
Au......	$18\cdot7$	$14\cdot3$	Se	$41\cdot5$	$43\cdot9$
Fe	$11\cdot9$	$11\cdot5$ (approx.)	Ag......	$18\cdot8$	18 (approx.)

The use of this relation simplifies Sieglerschmidt's to $qs^2V^{2\cdot55} = \text{constant}$, which is practically that already investigated. Observations are not sufficiently refined to decide whether the one-fifth power of the density is essential or not, and it seems best to retain the simpler forms already dealt with, and consider Sieglerschmidt's relation as a modified form of it.

(2) *Schaefer's Relations.*

If we express the new relation as $qV^x = Ce^{\beta\frac{\theta}{T}}$, the temperature coefficient of Young's Modulus is $\frac{\beta}{T}$, where T is the absolute temperature of fusion. That is, the temperature coefficient of Young's Modulus is inversely proportional to the melting temperature, a relation which accords well with that of C. Schaefer already noticed. The roughness of the rule, however, is illustrated by fig. 4, where the experimental values of the temperature coefficients are plotted against $\frac{1}{T}$.

Fig. 4.
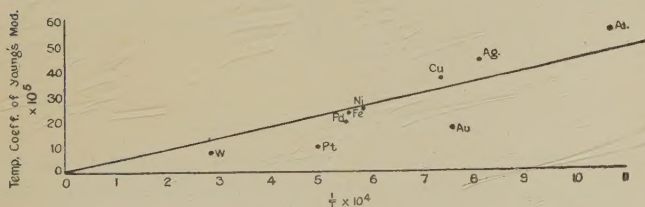
The fact that the coefficient of expansion is a function of the melting-point explains the relation between the coefficients of Young's Modulus and the coefficients of expansion.

Lejeune's Relation.

This has the form $q = 10Q$, where Q is the total amount of heat required to raise 1 c.c. of the substance to the melting-point and then liquefy it. This, if true, would be a very important relation between the internal energy of the substance and its elastic properties. The relation is derived from the properties of six metals and two alloys only, the specific heats of which are supposed to remain constant from room temperatures up to the melting-point. Now specific heats up to high temperatures for a large number of substances have been recorded by Eastman, Williams, and Young [*]; and these have been employed by the writer in a revised calculation in which the properties of twelve metals were used. As a result, the relation is found to disagree

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[*] Eastman, Williams, and Young, J. Amer. Chem. Soc. 1924, p. 1178.

with observation, whether the calculations are made from
0° C. to the melting-points (in which case $\frac{q}{Q}$ varies from
6·9 to 28·5), or from a given fraction of the absolute
temperature of fusion to the melting-point. In the latter
case, although $\frac{q}{Q}$ is much more nearly constant, it still
varies to the extent of 50 to 100 per cent. It seems
necessary on these grounds to consider the formula in-
applicable.

There remains only to mention the recent work of
W. M. Thornton on the relation between thermal conduc-
tivity, density, and Young's Modulus of Solid Electrical
Insulators. Since no useful addition to this work could be
made by the methods of this paper, the reader is referred to
the article itself for discussion[*].

Summary and Conclusions.

It is shown that of the suggested relations between
Young's Modulus and other physical constants, only that of
Clemens Schaefer between the temperature coefficients of
Young's Modulus and the melting-points is quite borne out
by experiment. A new relation, resembling that of Wert-
heim, between the atomic volume, absolute temperature of
fusion, and Young's Modulus, of the form $qV_x = Ce^{\beta\frac{\theta}{T}}$, is found
to be in wider agreement, includes Sutherland's relation as
a special case, and agrees with that of Schaefer. Two
values of the coefficients x and β are found, one for metals
below ·50 of the melting-point, the other for higher temper-
atures. The value of β cannot be stated accurately at
present.

[*] W. M. Thornton, Phil. Mag. xxxviii. p. 705 (1919).

LXXIII. *On the Surface-Tension Crystal* v. *Saturated So-lution. The concentration cell* :
   finely divided salt / supersaturated solution / saturated solution / large crystals. By LEO SOEP *.

AS the solubility of a crystal is, within certain limits, a function of the size of the crystal, the combination

   very small crystals/stronger, supersaturated solution/
                weaker saturated solution/large crystals

will form a concentration cell.

   And, indeed, Sauer † observed a potential difference be-tween two H_2Cl_2 electrodes—the one covered with very small crystals, the other covered with larger crystals. The former was negative against the latter one. The potential difference slowly decreased, and finally vanished, when the very small crystals grew larger ; just as was to be expected.

   In order to calculate the E.M.F. of the above-mentioned cell, we assume the number of crystals N to be the same on the left and on the right side. The smaller crystals are characterized by a normal n_{1i}, the larger ones by a corre-sponding normal n_{2i}.

   A very small quantity dW is dissolved from the smaller crystals. Work done (on the system) :

$$-N\Sigma\sigma_{1i}d\Omega_{1i},$$

if σ_{1i} means the surface-tension at the face belonging to the normal n_{1i}, and Ω_{1i} is the surface of that particular face.

   The same quantity dW is transferred osmotically from the stronger solution (1) to the weaker solution (2).

   Work done :

$$-\frac{RT}{M}.\ln\frac{c_1}{c_2}.d\text{W}.$$

(M is the molecular weight, c_1 and c_2 are the two solubilities.) The quantity dW crystallizes upon the larger crystals.

   Work done :

$$+N\Sigma\sigma_{2i}d\Omega_{2i}.$$

(We are supposing that all the crystals on the left side are changing in the same way, as well as the crystals on the right side, so that after the operation the left-hand crystals as well as the right-hand ones are still of equal sizes.)

* Communicated by the Author.
† Sauer, *Z. phys. Ch.* xlvii. p. 160 (1904).

The sum of the work done on the system :

$$S = -N\Sigma\sigma_{1i}d\Omega_{1i} + N\Sigma\sigma_{2i}d\Omega_{2i} - \frac{RT}{M}\ln\frac{c_1}{c_2}dW.$$

We have got to transform this equation before we can proceed. First of all, σ_{1i} must be equal to σ_{2i}.

Now we want to write the two sums $\Sigma\sigma_{1i}d\Omega_{1i}$ and $\Sigma\sigma_{2i}d\Omega_{2i}$ in such a form that dW is the unmeasurably small quantity, and not the increase or decrease of the crystal faces.

Before treating the general case, that is for any kind of crystals, we will consider the case of a cube, the simplest form of a crystal.

We suppose a crystal cube in equilibrium with its saturated solution. Afterwards it will be easier to treat the general problem.

Let us suppose a cube, edge a. If s be the specific weight, we have :

$$W = sa^3 = \text{the weight of the cube,}$$

$$\Omega = 6a^2 = \text{the surface of the cube.}$$

A very small quantity dW is dissolved from the cube, so that there remains a cube with an edge $a-da$, da being infinitely small. Then

$$dW = 3sa^2\,da,$$

$$d\Omega = 12a\,da,$$

$$\text{or} \quad d\Omega = \frac{4}{as}\,dW.$$

The surface forces tend to reduce the surface to a minimum. If the surface-tension is represented by σ, the work done by the surface forces, if dW is dissolved, is equal to $\sigma d\Omega$, or to $\frac{4\sigma}{as}dW$,

$$\sigma d\Omega = \frac{4\sigma}{as}\,dW.$$

Let us now consider the general case, a crystal in equilibrium with its mother liquor, but a crystal which may belong to the hexahedric class as well as to the triclinic one.

According to Valeton[*] the surface-tensions solid-liquid at the faces of a definite crystal in the equilibrium state are proportional to the lengths of the normals dropped from the centre of the crystal upon the facettes.

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[*] Valeton, *Verh. sächs. Ges. d. Wiss.* lxxvi. p. 1 (1915).

If σ_i is the surface-tension at the facette with the index i, n_i the normal dropped upon that facette, this rule may be expressed mathematically as

$$\sigma_i = n_i\sigma_0.$$

(σ_0 is a constant for any definite crystal.)

The weight of the whole crystal is W. We may divide the crystal into a number of pyramids by planes through the edges and the centre, then

$$W = \Sigma W_i,$$

W_i representing the weight of a pyramid, with base facette i.

$$W = \Sigma W_i = \Sigma \tfrac{1}{3} n_i \Omega_i s.$$

Also

$$\Omega = \Sigma \Omega_i = \Sigma k_i n_i^2. \quad (k_i \text{ is a constant.})$$

Therefore

$$dW = \Sigma \tfrac{1}{3} s\, d(\Omega_i n_i)$$

$$= \Sigma \tfrac{1}{3} s\, d\; k_i n_i^3)$$

$$= \Sigma k_i s n_i^2 dn_i,$$

$$d\Omega = \Sigma 2 k_i n_i dn_i.$$

Combined

$$dW = \Sigma \frac{s n_i}{2} d\Omega_i = \frac{s}{2} \Sigma n_i d\Omega_i.$$

The work done by the surface forces is

$$\Sigma \sigma_i d\Omega_i, \quad \text{or making use of } \sigma_i = n_i\sigma_0,$$
$$= \sigma_0 \Sigma n_i d\Omega_i.$$

So we get finally

$$\underline{\Sigma \sigma_i d\Omega_i = \frac{2\sigma_0}{s} dW = \frac{2\sigma_0}{s} \Sigma dW_i.}$$

Applying this formula to a cube, we get

$$n_1 = n_2 = n_3 = \frac{a}{2}, \qquad \sigma_1 = \sigma_2 = \sigma_3 = \sigma,$$

$$\Sigma \sigma_i d\Omega_i = \frac{4\sigma}{as} dW.$$

For a sphere, radius r, which we may consider as a

polyhedron with an infinite number of facettes,

$$n_1 = n_2 = n_3 = \ldots\ldots = n_i = r,$$

$$\sigma_1 = \sigma_2 = \sigma_3 = \ldots\ldots = \sigma_i = \sigma,$$

$$\underline{\Sigma\, \sigma_i d\Omega_i = \frac{2\sigma}{rs} d\mathrm{W}.}$$

Evidently σ_0 is a characteristic constant for any definite crystal, in equilibrium with its saturated solution. If the same material crystallizes in two or more different ways (rock-salt: cube and octahedra), we have to consider two or more σ_0's.

σ_0 is only a function of

1. The constitution of the molecules forming the crystal.

2. The kind of molecular lattice.

We go back to our starting-point, p. 676, and write down

$$\sigma_{1i} = (\sigma_0)_1 n_{1i} = \sigma_{2i} = (\sigma_0)_2 n_{2i}$$

$[(\sigma_0)_1$ and $(\sigma_2)_2$ are the constants for the two kinds of crystals].

If Ω_1 represents the total surface of the smaller crystals, Ω_2 that of the larger ones,

$$\frac{\Omega_1}{\Omega_2} = \frac{\Omega_{1i}}{\Omega_{2i}} = \frac{(n_{1i})^2}{(n_{2i})^2}.$$

Assuming that N is so large, and $d\mathrm{W}$ is so small (virtual process) that the proportion $\dfrac{n_{1i}}{n_{2i}}$ remains constant, we have therefore

$$\frac{d\Omega_1}{d\Omega_2} = \frac{d\Omega_{1i}}{d\Omega_{2i}} = \frac{(n_{1i})^2}{(n_{2i})^2},$$

$$\sigma_{1i}d\Omega_{1i} = (\sigma_0)_1 n_{1i} d\Omega_{1i},$$

$$\sigma_{2i}d\Omega_{2i} = (\sigma_0)_2 n_{2i} d\Omega_{2i},$$

$$\frac{\sigma_{1i}d\Omega_{1i}}{\sigma_{2i}d\Omega_{2i}} = \frac{d\Omega_{1i}}{d\Omega_{2i}} = \frac{(n_{1i})^2}{(n_{2i})^2}.$$

On the other hand,

$$\frac{n_{1i}}{n_{2i}} = \frac{n_{11}}{n_{21}} = \frac{n_{12}}{n_{22}} = \frac{n_{13}}{n_{23}} = \ldots \ldots,$$

$$\frac{(n_{1i})^2}{(n_{2i})^2} = \frac{(n_{11})^2}{(n_{21})^2} = \frac{(n_{12})^2}{(n_{22})^2} = \frac{(n_{13})^2}{(n_{23})^2} = \ldots \ldots,$$

$$\frac{(n_{1i})^2}{(n_{2i})^2} = \frac{\sigma_{1i}d\Omega_{1i}}{\sigma_{2i}d\Omega_{2i}} = \frac{\sigma_{12}d\Omega_{11}}{\sigma_{21}d\Omega_{21}} = \frac{\sigma_{12}d\Omega_{12}}{\sigma_{22}d\Omega_{22}} = \frac{\sigma_{13}d\Omega_{13}}{\sigma_{23}d\Omega_{23}} = \ldots \ldots$$

$$= \frac{\Sigma \sigma_{1i}d\Omega_{1i}}{\Sigma \sigma_{2i}n\Omega_{2i}},$$

$$\Sigma \sigma_{1i}d\Omega_{1i} = \frac{(n_{1i})^2}{(n_{2i})^2}\Sigma \sigma_{2i}d\Omega_{2i},$$

$$-\Sigma \sigma_{1i}d\Omega_{1i} + \Sigma \sigma_{2i}d\Omega_{2i} = \left\{ 1 - \frac{(n_{1i})^2}{(n_{2i})^2} \right\} \Sigma \sigma_{2i}d\Omega_{2i}.$$

So we may write for the sum of the work done by transporting dW from the smaller crystals through the solutions to the larger crystals:

$$S = N \left\{ 1 - \frac{(n_{1i})^2}{(n_{2i})^2} \right\} \Sigma \sigma_{2i}d\Omega_{2i} - \frac{RT}{M} \cdot \ln \frac{c_1}{c_2} \cdot dW.$$

But

$$\Sigma \sigma_{2i}d\Omega_{2i} = \frac{2(\sigma_0)_2}{s} \cdot dW,$$

and therefore

$$S = N \left\{ 1 - \frac{(n_{1i})^2}{(n_{2i})^2} \right\} \frac{2(\sigma_0)_2}{s} dW - \frac{RT}{M} \ln \frac{c_1}{c_2} dW.$$

In transporting $n\dfrac{dW}{M}$ equivalents through an element from the negative pole to the positive one, the electric work done amounts to

$$- EnF \frac{dW}{M}.$$

In our case the negative pole is on the side of the small crystals, the positive one on the other side.

Neglecting diffusion potentials, we have therefore

$$- \frac{EnF}{M}dW = N \left\{ 1 - \frac{(n_{1i})^2}{(n_{2i})^2} \right\} \frac{2(\sigma_0)_2}{s} \cdot dW - \frac{RT}{M} \ln \frac{c_1}{c_2} \cdot dW,$$

$$(\sigma_0)_2 = \frac{s}{2N \left\{ 1 - \dfrac{(n_{1i})^2}{(n_{2i})^2} \right\}} \left\{ \frac{RT}{M} \ln \frac{c_1}{c_2} - \frac{EnF}{M} \right\}.$$

Supposing that $\frac{c_1}{c_2}$ is independent of the temperature,

$$\frac{d(\sigma_0)_2}{dT} = \frac{s}{2N\left\{1 - \frac{(n_{1i})^2}{(n_{2i})^2}\right\}}\left\{\frac{R}{M}\ln\frac{c_1}{c_2} - \frac{dE}{dT}\cdot\frac{nF}{M}\right\}.$$

If L represents the molecular heat of solution, we have, according to the second Law of Thermodynamics,

$$L = A - T\frac{dA}{dT},$$

$$dW\cdot\frac{L}{M} = (\Sigma\sigma_{2i}d\Omega_{2i}) - T\frac{d(\Sigma\sigma_{2i}d\Omega_{2i})}{dT}$$

$$= \frac{2(\sigma_0)_2}{s}dW - \frac{2T}{s}\frac{d(\sigma_0)_2}{dT}dW,$$

$$\frac{L}{M}\cdot\frac{s}{2} = (\sigma_0)_2 - T\frac{d(\sigma_0)_2}{dT}.$$

From our formulæ

$$(\sigma_0)_2 - T\frac{d(\sigma_0)_2}{dT} = \frac{s}{2N\left\{1 - \frac{(n_{1i})^2}{(n_{2i})^2}\right\}}\cdot\frac{nF}{M}\left\{T\frac{dE}{dT} - E\right\}$$

$$= \frac{L}{M}\cdot\frac{s}{2}.$$

As $(\sigma_0)_2$ and $\frac{d(\sigma_0)_2}{dT}$ can be calculated from a set of observations on the concentration cell,

smaller crystals / stronger solution / weaker solution /
                                        larger crystals,

the last equation can be checked.

If n_{1i} is very small compared with n_{2i}, the equation takes the form :

$$(\sigma_0)_2 - T\frac{(d\sigma_0)}{dT} = \frac{s}{2N}\cdot\frac{nF}{M}\left(T\frac{dE}{dT} - E\right)$$

or

$$L = \frac{nF}{M}\left\{T\frac{dE}{dT} - E\right\}.$$

(It is not necessary to neglect the variation of $\frac{c_1}{c_2}$ with the temperature ; only the final formula becomes much simpler.)

REFERENCES:—Wulff, *L. f. Kryst.* xxxiv. p. 512 (1901).   Hilton, ' Mathematical Crystallographie,' Oxford, 1903.   Liebmann, *L. f. Kryst.* liii. p. 171 (1914).

LXXIV. *Projective Geometry of Galileian Space-Time.*
By L. Silberstein, *Ph.D.*[*]

1. FROM the differential metrical view-point, commonly adopted, the space-time in absence of gravitation, as treated in special relativity theory, or briefly Galileian space-time is characterized as a four-space of *constant Riemannian curvature*, viz. zero.

According to a famous theorem due to F. Schur [†], every space of constant Riemannian curvature is a *projective* space, and conversely.

The aforesaid space-time is, therefore, a projective four-fold, and it is precisely the purpose of this paper to present it in a projective or non-metrical treatment.

2. The primitive concepts or undefined elements of projective geometry are *points* and *lines* (as a short for "straight lines"). The former will be here replaced by *world-points*, which call for no classification, there being no difference whatever between a given world-point and any other (homogeneity of the world). The latter will be replaced by lines of three kinds : *time-lines*, singular or *light-lines*, and *space-lines*. Of these the first will stand for world-lines of free particles, each representing, that is, uniform motion of a particle. Needless to say, "uniform motion" is not to presuppose "distance," measured "time" and "velocity" as their quotient, but to be taken as an undefined element, such as "line" in projective geometry. The second, a limiting case of the first, will be the world-lines of light-signals. Finally, the lines of the third kind will be ordinary straight space-lines, continua of world-points which are, or rather *can* be made, simultaneous. The reader may take the last as one more undefined term. A more satisfactory way of putting the matter is this. Having borrowed from geometry all lines, and having specified physically the first two kinds, let us proceed by exclusion and call space-line every line that is neither a time-line nor a light-line.

[*] Communicated by the Author.

[†] Friedrich Schur, *Mathem. Annalen*, vol. xxvii, pp. 536–567 (1886), especially Theorems IV. and V. The extension from three to four or more dimensions offers no difficulty, and the non-definiteness of the quadratic form of the manifold in hand carries only with it the necessity of distinguishing between space-like, time-like, and singular straight lines which will be taken care of presently. Due to this distinction also is the main *physical* interest of our subject. For otherwise we would, though in physically sounding words, be merely talking of the usual projective space.

In diagrams all the three kinds of lines will be constructed by means of a straight-edge, special distinguishing marks being used whenever needed. It is scarcely necessary to add that all our constructions have to be made with the aid of a straight-edge alone, neither a measuring rod (or only a " parallel ruler ") nor transportable clock mechanisms being allowed by the very nature of the proposed treatment. In other words, we must divest our minds from any quantitatively comparable distances, angles and time intervals.

The Galileian world being projective, all the usual axioms of projective geometry * will be taken to hold for all these world-points and lines. Thus, through every pair of world-points will pass one and only one line, their join, time-like, space-like or singular. A world-plane will be obtained by drawing a pencil of lines through A to all the points of the join of two other points B, C, not collinear with A. Every two coplanar lines, whether of the same or of different kinds, will meet in one and only one point, their cross, and so on.

3. As the extension to three and to four dimensions is obvious, it will be enough to consider in some detail a flat sub-manifold of the world of two-dimensions, a space and a time-dimension, that is. It is well known the theorem of Desargues,

> If two triangles are perspective from a point,
> they are perspective from a line, and conversely,

does not follow from the axioms of projective geometry for a plane as such. But if the latter be a " part " or rather a sub-manifold of only a three- or four-dimensional projective space, as in the present case, the theorem of Desargues, of paramount importance in our connexion, holds for the plane in question and ensures the determinateness of constructions such as of harmonic elements, without the need of ever leaving that plane.

4. Time-lines and light-lines have, each, a natural positive sense, from past to future, and will be arrowed accordingly in our diagrams. Not so the space-lines, however, which have no sense, unless one is artificially impressed upon them. Such will be the case whenever we shall speak of vectors. These, of all three kinds, will be technically very

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* Say, Schur's set of six axioms, with the extension to four dimensions and the projective form of the Archimedean postulate. *Cf.*, for instance the writer's ' Projective Vector Algebra,' London, Bell, 1919, Note to p. 2, and footnote on p. 3. This booklet will be briefly referred to as P.V.A.

convenient. A projective vector $\overrightarrow{OA}$ or briefly OA is an ordered pair of points, O its origin, and A its end-point. In the present case, according to the kind of the line joining O and A, such a vector will be called time-like, singular, or space-like. As in P.V.A., two vectors OA and $O'A'$ (fig. 1) are defined as *equal* if, and only if, they are contained between two pairs of lines meeting at a fixed line, any line

Fig. 1.
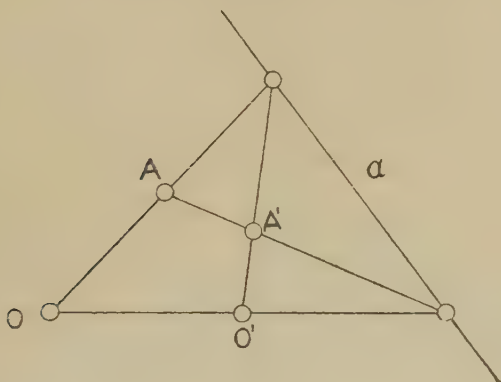
of the plane arbitrarily chosen as a reference line. The latter will be called throughout *the a-line*. Without such an auxiliary line (replacing the usual "line at infinity") no such comparison of non-metrical vectors is possible *.

Henceforth our Galileian world will consist of all points of the drawing plane with exception of those of the *a*-line itself.

This definition of vector equality is an obvious generalization of the usual one. It is important to notice that it enjoys the property of transitivity, that is to say, if we have the two vector equalities

$$OA = O'A', \quad O'A' = O''A'', \quad . \quad . \quad . \quad (1)$$

then also, by Desargues' theorem,

$$OA = O''A''. \quad . \quad . \quad . \quad . \quad (2)$$

For the triangles $OO'O''$ and $AA'A''$ (fig. 2) are perspective, from S, and since by (1) two pairs of corresponding sides

* It will be seen in the sequel that a simple device will ensure automatically that only vectors of *equal kind* (both time-like, or singular, or space-like) can be equal to each other in the explained sense of the word.

2 Y 2

intersect on the *a*-line, such will also be the case of the third pair, which means the equality (2). Notice that in this case the line of perspectivity (*a*) passes through the point of perspectivity (*S*), which is a special case of Desargues' theorem. In much the same way the reader will see that the vector equalities $AB = A'B'$ and $BC = B'C'$ always imply $AC = A'C'$. Again, the said transitivity enables us at once to construct a vector $O'A'$

Fig. 2.
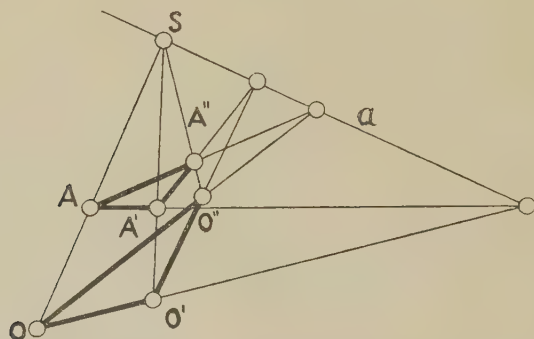
equal to OA and collinear with it (by two such transfers from line to line) and in particular, if $O' \equiv A$, to construct $OA' = OA + OA$, the double of OA, and so on, as shown in all detail in P.V.A.

For the subject aimed at the reference or *a*-line will be seen presently to be also otherwise very helpful, nay indispensable.

5. In fact, suppose we abstained even, for the time being, from comparing vectors or pairs of world-points at all, but desired only to represent graphically the barely qualitative feature of the existence of time-like and space-like lines and of light-lines separating them. Let O represent a world-point and l_1, l_2 the two light-lines passing through it, dividing the plane into the domains of time-like and space-like lines, as shown in fig. 3. Thus far nothing else is needed. Suppose, however, we wish to fix our attention in turns upon other and other world-points O', O'', and so on. The knowledge of the light-lines through O does not help us at all to draw the light-lines through O', O'', etc. (In the usual, metrical presentation these are simply drawn " parallel " to each other, a concept foreign to our circle of ideas.) Are we then to draw the light-lines for each new origin afresh, quite arbitrarily and independently of each

other? Such a representation would soon lead to utter confusion and would scarcely be of any use.

Fig. 3.
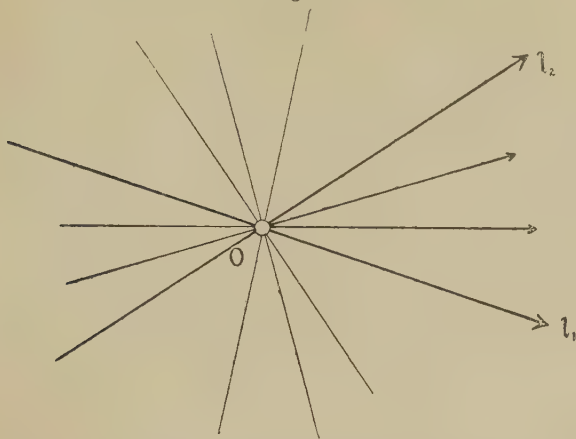
Let, however, an *a*-line be drawn across the plane (not through *O*), cutting the previous light-lines l_1, l_2 in L_1, L_2 respectively (fig. 4). Then, consistently with the preceding

Fig. 4.
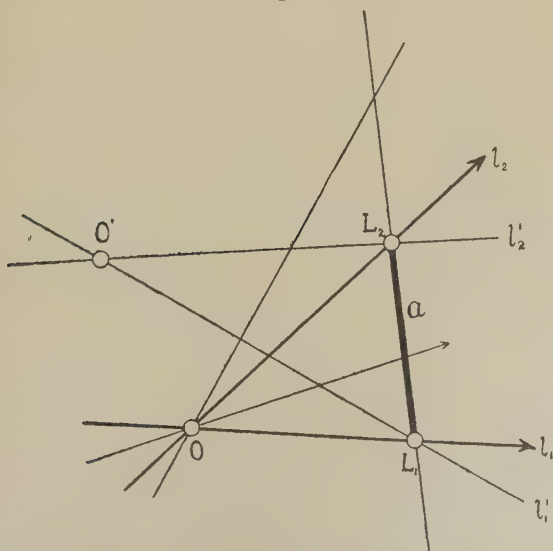
definition of vector equality, the light-lines $l_1{}'$, $l_2{}'$ for another origin O' will be the lines joining O' with L_1 and L_2. Similarly for all other points, O'', O''', etc., those of the

a-line itself being always excluded. Henceforth we can drop all those light-lines and mark only the two points L_1, L_2, any two points on the *a*-line, to serve once and for all as the "termini" of light-lines belonging to any world-point as origin.

The complete reference skeleton will thus consist of an arbitrarily fixed *a*-line and two points. L_1 and L_2, marked on it as well as the segment L_1L_2 (drawn heavily in fig. 4) to distinguish it from the supplementary segment, completing the *a*-line which, as every projective line, is closed.

Any line crossing the first segment will then be time-like, any passing through the supplementary segment will be space-like, while those passing through L_1, L_2 themselves will be light-lines, representing the propagation of light-signals up and down the one-dimensional abode of an observer. Recalling the previous definition, it will now be seen that two vectors can be equal only when they are of the same kind.

Fig. 5.
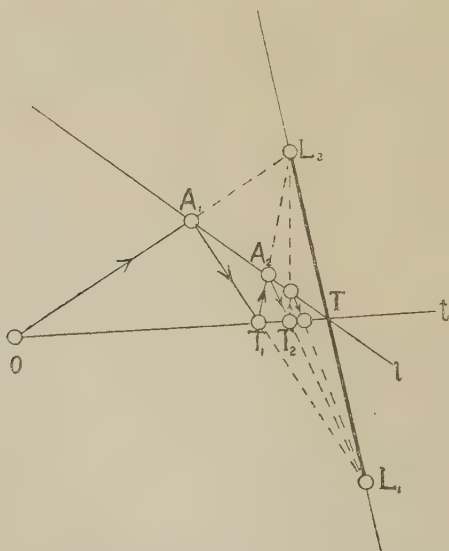
If O be any world-point, $t = OT$ a time-line and $s = OS$ a space-line through it, the two pairs of lines, t, s; l_1, l_2 *separate* each other in the strict sense of the word. And so also do, of course, the two pairs of points, T, S; L_1, L_2.

6. *Any* time-line t or OT (fig. 5) can represent the history of an observer "at rest." If thus viewed, it will be his own time-axis, and successive points marked on it will

represent successive time instants of his own history, with O as the origin of his time reckoning, say, $t=0$, but without the possibility as yet of assigning time values to other instants or points of that axis.

Any other time-line t' passing through O will represent the (uniform) motion of a free particle or of another observer, who at $t=0$ coincided with the former. The second observer will be "at rest" simply by declaring the line t' as time-axis. But these remarks are too familiar to be any further insisted upon.

What interests us next is some other particle, station, or observer permanently at rest relatively to the first observer. Such will manifestly be represented by a line, say l, passing through T. Now, to establish his time-scale, let the first observer send a light-signal to the second, which will be represented by the segment OA_1 of the line OL_2. Let this signal be reflected to the first observer, thence again to the second, and so on, giving rise to the points T_1, T_2, etc., crosses of A_1L_1, A_2L_1, etc. with the t-axis, representing the instants of the first, second, etc. return of the light-signal. Now, by construction, the vector OT_1 is equal to A_1A_2 and this to T_1T_2, and so on. Thus also the (collinear) vectors OT_1, T_1T_2, T_2T_3, etc. are all *equal* to each other. (In fact, this construction, representing to-and-fro signalling between a pair of stations in relative rest, does not differ from the usual construction of the Staudtian projective scale.) To this sequence of points then we will give the time-labels $t=1$, 2, 3, etc., and we will say that the *time-intervals* from O to T_1, from T_1 to T_2, and so on, are all equal. All this in the name of the previous definition of vector equality. But this arrangement is also otherwise agreeable, because O, T_1, T_2, etc. represent the sending, the first return, the second return, etc. of the light signal, and as the two stations are at relative rest, such an equality definition of time intervals is but natural, being merely equivalent to declaring the sameness of light propagation in the course of time.

In this way, O and T_1 only being chosen arbitrarily (origin and unit of time), the time-scale of our observer is established in a perfectly definite manner[*]. Needless to say, the point T itself will have the label $t=\infty$ (on one, and $t=-\infty$ on the other side of the a-line), and negative labels will be assigned to world-points beyond the a-line and to the left of O, these forming but one connected domain.

[*] The inclusion of negative, fractional, and irrational t-values offers no difficulty. For details of construction see P.V.A. or any modern treatise on projective geometry.

7. The time-scale being thus established on the line OT_∞, we may draw any space-line whatever OX_∞ to serve as x-axis, *i. e.* to represent all the points of the one-dimensional space at the instant $t = 0$ or all world-points simultaneous with O, from our observer's point of view. On this arbitrary axis, chosen without any attention to the light-lines, a Staudtian scale of points X_n with the corresponding space-coordinates $x = n$ could again be set up. Then the projective coordinates x, t of any point P of the world would be determined in the well-known way by the two joins $T_\infty P$ and $X_\infty P$ (fig. 6), the former finding the x-value on the space-

Fig. 6.
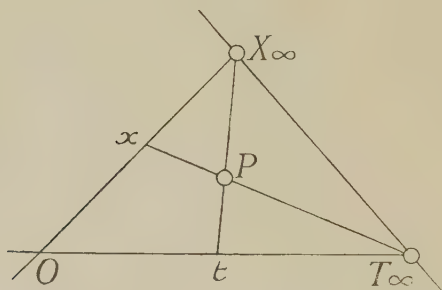
axis and the latter the t-value on the time-axis. In these coordinates any line through O, and thus also the light-lines, will have an equation of the form $x/t = \text{const.}$, and by a proper choice of the point X_1 we can always make the equation of the light-line OL_2, say,

$$x = t.$$

But then the other light-line OL_1 will, in general, *not* be represented by $x = -t$, which, however, should obviously be required, since these two lines represent light-signalling up and down a one-dimensional space. Can this requirement be satisfied at all. and if so, how must the space-axis or the point X_∞ be chosen to fulfil it? To answer this question, draw the line $X_\infty T_1$, and let this cut OL_2 in P and OL_1 in Q (fig. 7). Draw $T_\infty P$, and let its cross with OX_∞ be our unit point X_1. This will give to P the coordinates $x = t = 1$, and therefore, to the light-line OL_2 the equation $x = t$. Next, draw the line $T_\infty Q$ and take its intersection with the space-axis as our scale-point X_{-1}. This will ensure for the light-line OL_1 the desired equation

$$x = -t.$$

But $X_{-1} O X_1 X_\infty$ is an harmonic range. Such, therefore, is also $Q T_1 P X_\infty$, being the former projected from T_∞. Consequently, $L_1 T_\infty L_2 X_\infty$, which is the projection of the latter range from O, must again be an harmonic range, with $X_\infty T_\infty$ and $L_2 L_1$ as pairs of conjugates. This necessary condition is also the sufficient one.

Fig. 7.
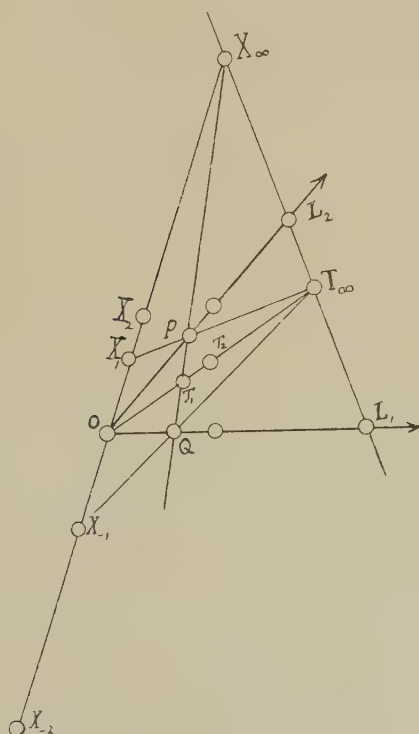
In fine, if the equations of the light-lines are to be

$$x = t \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{OL}_2)$$

and $$x = -t, \quad . \quad . \quad . \quad . \quad . \quad (\text{OL}_1)^*$$

the space-axis OX_∞ *must be conjugate to the time-axis* with respect to the light-lines, and conversely.

Henceforth the space axis (OX_∞ or OX'_∞, etc.) corresponding to an arbitrarily fixed time-axis (OT_∞, OT'_∞, etc.) will always be so chosen. In other words, X_∞, X'_∞, etc. will

* Or, more generally, $x = at$, $x = -at$, where a is any constant.

be conjugate to T'_∞, T''_∞, etc. with respect to the two light-points L_1, L_2 fixed once and for all. (Needless to say, if T_∞ approaches L_2, so does X_∞. Similarly for L_1.)

· The three basal points O, X_1, X_∞ being thus fixed, the whole x-scale is co-determined by the Staudtian construction, giving X_2, X_{-2}, etc. as uniquely determined points. In fig. 7 these points are so constructed as to exhibit that $x = \pm 2$ are reached for $t = 2$, by light-signalling from O.

The equation of any time-line through O, representing the (uniform) motion of a free particle, will now be

$$x = vt, \quad |v| < 1,$$

and that of a space-line $x = pt$, $|p| > 1$, with unity as the limiting absolute value of these constant coefficients. In the former case the coefficient v, giving the number of projective steps covered per unit time, can be simply called the velocity of the particle relative to the station or the observer whose world-line is OT_∞.

8. Our next duty is to consider the transformation of coordinates x, t into x', t', corresponding, that is, to two systems or observers in uniform relative motion to each other. Each pair of axes being conjugate with respect to the light-lines OL_1, OL_2, this transformation corresponds simply to the passage from one such pair to another pair of conjugate axes, and could be rapidly written down. But in order to see clearly the meaning of the symbols (and especially that of a certain factor which in a non-metrical treatment must remain free) it will be instructive to proceed step by step

Let the dashed system S' move relatively to S with the uniform velocity v, that is to say, let the S-equation of the t'-axis be

$$x = vt. \quad . \quad . \quad . \quad . \quad . \quad (OT'_\infty)$$

Let P be any world-point. Then its coordinates $t = \tau$, $x = \xi$ will be found by drawing PX_∞, PT_∞, and similarly its coordinates t', x' by drawing PX'_∞, PT'_∞, as shown in fig. 8. The equation of the line PX'_∞ is

$$(x - \xi) + \lambda(t - \tau) = 0, \quad . \quad . \quad . \quad (PX'_\infty)$$

where λ is a constant, and, therefore, the S-time of the point $Q = PX'_\infty \cdot OT'_\infty$,

$$t_Q = \frac{\xi + \lambda\tau}{v + \lambda}.$$

Notice that by definition this is the t-label of the point of OT_∞ cut by $X_\infty P$. What we require, however, is t' or $t_{Q'}$,

i. e. the label of the projection (from X_∞) of the former point on the axis OT''_∞. Now, *the ratio of these two numerical labels is perfectly arbitrary* *, say,

$$t_Q' : t_Q = \alpha(v),$$

where α has for all pairs of corresponding points the same value which, however, may be any function of the coefficient v, subject only to the condition $\alpha(0) = 1$. Thus we have

$$t' = \alpha(v) \frac{\xi + \lambda\tau}{v + \lambda}.$$

Fig. 8.
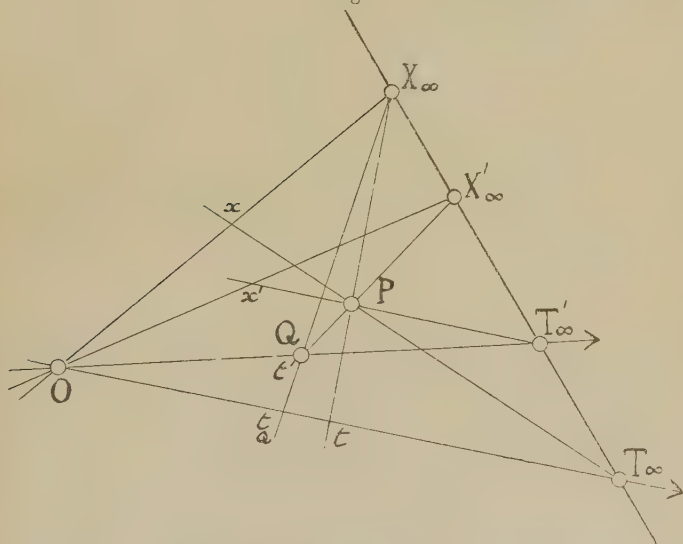
In quite the same way, writing $x = t/q$ for OX'_∞ and $(x - \xi) + \mu(t - \tau) = 0$ for PT''_∞, we shall find

$$x' = \beta(v) \frac{\xi + \mu\tau}{1 + \mu q},$$

where $\beta(v)$ is another free factor. Thus, replacing again ξ, τ by x, t, the transformation formulæ become

$$t' = \frac{\alpha(x + \lambda t)}{v + \lambda}, \quad x' = \frac{\beta(x + \mu t)}{1 + \mu q}. \quad . \quad . \quad . \quad (1)$$

x', t' are linear homogeneous functions of x, t. Between

* For we have thus far introduced no metrical comparison of coinitial non-collinear vectors. In other words, having chosen a time unit on OT_∞, the choice of unit on OT'_∞, and on other axes, OT''_∞, etc., remains entirely free.

the several freely introduced coefficients there are four relations. First, the line OT'_∞ or $x' = 0$ was written also $x = vt$, whence, by the second of (1),

$$\mu = -v \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Second, the line OX'_∞ or $t' = 0$ was written $t = qx$, whence, by the first of (1),

$$\lambda q = -1 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Third and fourth, X_∞ and T_∞ as well as X'_∞ and T'_∞ being conjugate with respect to the light-points, the equations $x = \pm t$ are transformed into $x' = \pm t'$, respectively, so that, by (1) and (2),

$$\frac{\beta(1 - v)}{1 - vq} = \frac{\alpha(\lambda + 1)}{v + \lambda},$$

$$\frac{\beta(1 + v)}{1 - vq} = \frac{\alpha(\lambda - 1)}{v + \lambda},$$

whence $\dfrac{\beta}{1 - vq} = \dfrac{\alpha\lambda}{v + \lambda}, \quad \dfrac{\beta v}{1 - vq} = -\dfrac{\alpha}{v + \lambda}.$

These equations together with (3) give

$$q = -\frac{1}{\lambda} = v, \quad \beta = \alpha.$$

Notice in passing that the equation of OX'_∞ thus becomes

$$t = vx,$$

while that of OT'_∞ is

$$x = vt.$$

Ultimately, therefore, the transformation formulæ (1) become

$$x' = \frac{\alpha(x - vt)}{1 - v^2}, \quad t' = \frac{\alpha(t - vx)}{1 - v^2}. \quad . \quad . \quad . \quad (4)$$

These contain the only undetermined and perfectly arbitrary factor α whose geometrical meaning is expressed by

$$\alpha = t'_{A'} : t_A = \text{constant along the point range } A, \quad . \quad . \quad (5)$$

A being any point of OT_∞ and A' its projection from X_∞ upon OT'_∞. It is important to keep in mind this original meaning of the factor α which, apart from metrics, may be any function of the coefficient v or the velocity of the two systems, subject to the only condition $\alpha(0) = 1$ *.

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* Needless to say that for $a = \sqrt{1 - v^2}$ the transformation (4) of our projective coordinates assumes exactly the form of the Lorentz transformation. But we must not hasten to give it that shape.

Before leaving this subject, one more remark. Solving (4) for x, t, we have

$$x = \frac{1}{\alpha}(x' + v't'), \quad t = \frac{1}{\alpha}(t' + v'x'). \quad . \quad . \quad (4\,a)$$

But it would be rash to conclude, in imitation of the common treatment, that this, with the requirement of symmetry (reciprocity) of the two systems, calls for $\alpha^2 = 1 - v^2$, leading to the usual Lorentz transformation. In fact, if we repeated the whole of the preceding reasoning, starting from T'_∞, X'_∞ and passing to T_∞, X_∞, we should find

$$x = \frac{\alpha'(x' - v't')}{1 - v'^2}, \quad t = \frac{\alpha'(t' - v'x')}{1 - v'^2}, \quad . \quad . \quad (4')$$

where the arbitrary factor would have the meaning

$$\alpha' = t_\mathrm{B} : t'_{\mathrm{B}'} = \mathrm{const.}, \quad . \quad . \quad . \quad . \quad (5')$$

B' being any point of OT'_∞ and B its projection from X'_∞ upon OT_∞. What we thus know is that (4') must be identical with (4 a), and this gives only $v' = -v$ (as might have been expected) and

$$\alpha\alpha' = 1 - v^2. \quad . \quad . \quad . \quad . \quad (6)$$

There is, however, no particular reason for putting $\alpha = \alpha' = \sqrt{1 - v^2}$. There is symmetry between the two systems anyhow, automatically. Choosing $\alpha = \sqrt{1 - v^2}$ amounts to impressing metrics upon the manifold, with $t^2 - x^2 = 1$ as "the metrical unit curve" [*]. Then and only then have we, by (4) or (4'), the metrical invariant $t^2 - x^2 = t'^2 - x'^2$, whereas without any such metrical device not the expression $t^2 - x^2$ is invariant but the equation $t^2 - x^2 = 0$ or, what is more stringent and from the present point of view more instructive, the equations of the two light-lines, $x - t = 0$ and $x + t = 0$. It is scarcely necessary to add that from the physicist's point of view a common factor such as α is a matter of indifference.

The preceding developments exhaust all that is essential about the two-dimensional case, the answers to any particular

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[*] In other words, the scale-points $T_{(1-v^2)^{-\frac{1}{2}}}$, each on its line $x = vt$, are then considered as "equidistant" from the world-point O, and $\sqrt{dt^2 - dx^2}$ becomes "the distance" or "the interval" between world-points of projective coordinates t, x and $t + dt$, $x + dx$.

The metrical curve $x^2 - t^2 = 1$ is the hyperbola in Minkowski's representation of the Lorentz transformation. Since, in our treatment, it has two points (L_1, L_2) in common with the a-line (which plays the rôle of "the line at infinity") it deserves also from our point of view the name of an hyperbola. *Cf.* Veblen and Young's 'Projective Geometry,' vol. ii

questions concerning it being easily deducible from what was said above.

9. *Three-dimensional world.*—Although, as was said in section 3, the detailed treatment of the two-fold (t, x) is sufficient for a thorough grasping of the projective treatment of a Galileian world, yet the next higher manifold (t, x, y) offers a few points of particular interest which may justify the inclusion of the present section.

Instead of an a-line our reference element will now be a world-plane which may be shortly referred to as the plane α. The Galileian three-world will now consist of all points with

Fig. 9.
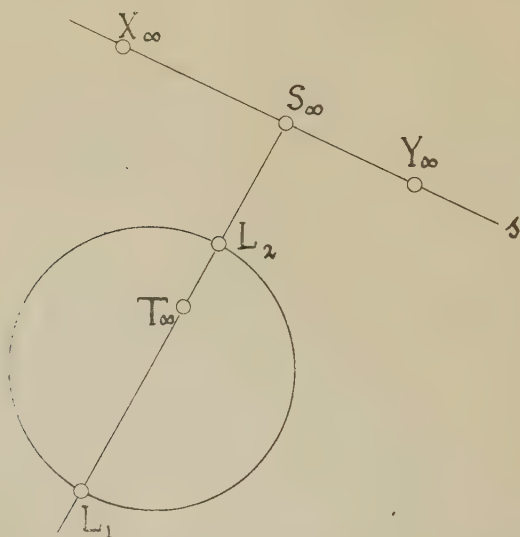
the exception of those of the α-plane. On this plane we will imagine drawn once and for all a closed curve l, to begin with, *any* closed line, dividing α into two domains, a time-domain and a space-domain. All lines crossing α in any point T_∞ of the former will be time-like, and all those piercing it in any point S_∞ of the latter domain will be space-like, while those passing through an l-point will be singular or light-lines. Thus, from any world-point O a whole cone of light-lines, subtended by the *light-curve l*, will issue. Such a cone will represent light propagation from and around O in a space-plane laid through this point. This plane will cut α in a line s (fig. 9). The origin O

being chosen, its reference system will be entirely fixed by marking T_∞, the terminus of the time-axis, and X_∞, Y_∞, the termini of the two space-axes. (The axes themselves need not be drawn. All that is needed are their termini.) As before, let the axes OT_∞, OX_∞, OY_∞ be provided with Staudtian scales of points T_m, X_n, Y_p, and let their indices be taken as the projective coordinates t, x, y of the system.

To begin with, s, the trace of our observer's space, might be chosen arbitrarily, provided it does not cut the curve l. Let us require, however, as for the two-dimensional world, that light propagation up and down the axis OX_∞ or any other line OS_∞ should be represented by the same law, *i. e.* by $x = t$ and $x = -t$, respectively, in general, by $s = t$ and $s = -t$. (Uniformity or reversibility of light propagation.) Then, as before, S_∞ must be conjugate to T_∞ with respect to L_1, L_2, the crosses of $S_\infty T_\infty$ with the light-curve l. But this must hold for every point of the line s. Moreover, claiming the same symmetry of light-signalling for any other system $O' T'_\infty X'_\infty Y'_\infty$, *i. e.* for any other pair of elements T'_∞ and s', the same property must hold for the points of any other line s' of the space-domain of α in relation to T'_∞ and always with respect to the same curve l. But this correlation is a genuine *polarity*, and we have the following result :—

The light-curve l will necessarily be a conic and s, the trace of the system-space, will be the polar of T_∞, the terminus of the corresponding time-axis, with respect to this conic. Conversely, T_∞ will be the pole of s with respect to l.

Notice that what is thus co-determined by the choice of the time-axis or T_∞ is *the space* (plane) or its trace s, but not the space axes or the points X_∞, Y_∞. The choice of these on the line s is, of course, a matter of indifference *.

This is one point of interest which follows with remarkable simplicity from the said requirement of symmetry, apparently a harmless assumption. But there is more, which follows with equal ease. In fact, since l is a conic, the section of the cone Ol by any world-plane π will again be a conic c. In particular, let π be a space-like plane (whose α-trace, that is, does not intersect l), say, that passing through the line s, and a point T_t of the time-axis. This plane will be our observer's two-space, the plane in which he lives, at the instant t, and the conic c, an ellipse, will be the locus of the points reached at that instant by the light-signal

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* This is as irrelevant as, say, the choice of oblique or rectangular space axes in the common treatment of special relativity.

emitted from the origin at the instant $t = 0$, or the wave-front. Thus the light will spread out around the source in ellipses. (Needless to say, there is, projectively, no distinction possible between a circle and any other ellipse, nor is there any need for such a distinction from the present point of view.)

Similarly as in the two-dimensional case, any line $O'T_\infty$ pointing to T_∞ will represent a station at permanent rest relatively to our observer or to the station represented by the world-line OT_∞.

On the other hand, any time-line OT_∞' will represent a particle moving uniformly relatively to the first system. The equations of its motion in projective coordinates will be $x = ut$, $y = vt$, where both constants u and v are smaller than or at the utmost equal to unity. An observer may be put into the place of this particle. Then OT_∞' will be his time-axis, and his two-space will be the plane Os', where s', a line on the α-plane, is the polar of T_∞' as pole, with respect to the conic l. Thus also the transformation from t, x, y to t', x', y' will amount to passing from one pole and its polar, T_∞, s, to another pole and its polar T_∞', s', always with respect to the same conic l. The writing down of the transformation formulæ may be left to the reader.

In the case of the full space-time of four dimensions the rôle of the α-plane will be taken over by a three-space Σ, divided by a closed surface λ into the time-domain Σ_T and the space-domain Σ_S, the former being allotted to the termini T_∞ of time-lines, and the latter to termini S_∞ of space-lines. If O be any world-point, outside Σ, and OT_∞ a time-axis through it, the corresponding three-space will cut Σ in a plane σ. The latter will contain X_∞, Y_∞, Z_∞, the termini of the three space-axes which may be chosen arbitrarily. If, however, the previous light symmetry be claimed, the surface λ must be a quadric, say ellipsoid, and σ will be the polar plane of T_∞ with respect to this quadric, any line OL piercing λ being a light-line. The transformation from one to another system moving uniformly with respect to it will amount to passing from one point (pole) T_∞ and its polar plane σ to any other pole T_∞' and polar σ' with respect to the same quadric λ. All details may be left to the reader.

Rochester, N.Y.,
    December 6, 1924.

LXXV. *On the Molecular Scattering of Light in Liquids.*
By K. S. Krishnan[*].

1. *Introduction.*

THE theory of molecular scattering of light in liquid media has been worked out recently by Raman[†], Ramanathan[‡], Gans[§], and others. Their results in general indicate that in a medium consisting of anisotropic molecules, there is, in addition to the polarized scattering due to density fluctuations, a scattering due to the optical anisotropy of the molecules of the liquid. The total intensity of the light scattered in a direction perpendicular to the direction of the incident light is given by the formula

$$I = \left\{ \frac{\pi^2 R T \beta}{18 N \lambda^4} (n^2 - 1)^2 (n^2 + 2)^2 \right\} \times \frac{6(1 + r)}{6 - 7r}, \quad . \quad (1)$$

where I is the fraction of the incident light scattered transversely, per unit volume, per unit solid angle,

n is the refractive index of the medium,

λ is the wave-length of the incident light,

T is the absolute temperature,

R and N are the gas const. and Avogadro number respectively per gm. molec.,

β is the isothermal compressibility, and

r is the observed depolarization of the transversely scattered light.

The expression inside the double brackets, which can easily be recognized as the Einstein-Smoluchowski formula, gives the density scattering, and $\frac{6(1 + r)}{6 - 7r}$ is the multiplying factor to be applied to that expression in order to take into account the anisotropy of the molecules. The theory of Raman and Ramanathan connects r with the optical anisotropy of the molecules in the gaseous condition, while that of Gans connects it with the observed value of electric double refraction (Kerr constant) of the liquid.

The experimental results so far available regarding the

[*] Communicated by Prof. C. V. Raman, F.R.S.

[†] Raman, ' Molecular Diffraction of Light,' Calcutta, 1922 ; Raman & Ramanathan,[*] Phil. Mag. xlv. p. 213 (1923); Raman & Rao, Phil. Mag. xlv. p. 625 (1923).

[‡] Proc. Ind. Assn. Cultn. Sc. viii. pp. 1–22 & 181–198 (1923).

[§] *Zeits. f. Phys.* xvii. p. 353 (1923).

intensity and depolarization of the light scattered by liquids are meagre. only about 15 liquids having been studied by Martin and Lehrman * and Raman and Rao †. It was therefore felt that a more comprehensive experimental work was desirable, especially in order to determine more clearly the influence of the molecular constitution of the liquid. This paper describes a series of such measurements on the intensity, and the depolarization for different regions of the spectrum, of light scattered by about 65 liquids, with a general discussion of the results.

2. *Experimental Details.*

In drawing up the list of liquids to be examined, care was taken that most of the important groups might be fairly represented. The liquids were all Kahlbaum's pure chemicals except ortho- and para-xylenes, which were Merck's extrapure, and benzyl alcohol which was obtained from a local firm. The liquids were directly transferred from the freshly opened bottles to the cleaned and dried bulbs in which they were to be examined (which were essentially of the same pattern as those used by Martin and later investigators) ; the bulbs were then exhausted and sealed. But no special precautions were taken in order to dry the liquids, since extreme drying was not considered necessary ‡.

The liquids were then obtained dust-free in one of the bulbs by repeated slow distillations and washing back to the other bulb. The liquids were tested for absence of dust particles by placing the bulb, immersed in water, at the focus of a powerful lens concentrating the rays reflected from the sun and looking against the transmitted light at a slight angle, when any dust particles floating in the liquid were brilliantly illuminated and could easily be detected.

In general, 4 or 5 distillations were sufficient to get the liquid perfectly dust-free, but in the case of methyl acetate, acetaldehyde, and some of the chlorides and bromides a larger number of distillations was necessary. In this respect water showed such a strong tendency to carry over dust particles in the process of distillation that the following special arrangements had to be made. A double bulb of the same pattern as in the other liquids but of pyrex glass, with the transverse connecting tube specially long and narrow,

* Journ. Phys. Chemistry, xxvi. p. 75 (1922).

† Phil. Mag. xlv. p. 625 (1923).

‡ In the case of benzene it was found that extreme drying in contact with phosphorus pentoxide for several months had very little effect on either the polarization or the intensity of the scattered light.

contained the liquid, which had originally been distilled over alkaline permanganate. The liquid was also distilled extremely slowly by keeping the bulbs at the room temperature and temperature of ice respectively. In spite of these precautions, the distillation had to be repeated more than a dozen times in order to get the water dust-free. After distillation the bulb had been allowed to stand for more than three months, and when examined later it was surprising to find that it contained such a large number of particles that it had to be redistilled before the experiment.

The bulbs were put away in suitable light-tight shelves, specially made for the purpose, so as to avoid continual exposure to the action of light.

The measurements were carried on inside a dark room into which a horizontal beam of sunlight was reflected by means of a heliostat of the single mirror type, through a small opening in the door. For observations on the imperfection of polarization of the transversely scattered light, the beam was concentrated by a lens of 20 cm. focal length whose aperture was limited to a small square portion at the centre, the actual size of the aperture varying, within certain limits, according to the intensity of the light scattered by the liquid, the object being to work with the smallest intensity consistent with the requisite amount necessary for accurate comparison. The largest aperture used (and that was while working with feebly scattering liquids like water and the alcohols or with coloured filters) was 2 cm. sq., while in other cases it was less, the usual size being 1·4 cm. sq.

The bulb containing the distilled liquid was blackened completely, excepting for three small windows—one for the entrance of light, one for its exit, and the third for observation. It was immersed in a small rectangular tank of distilled water (whose outside was also blackened, leaving similar openings), so as to minimize reflexion from the sides of the bulb. The position of the bulb was adjusted so that the rays might pass axially through the bulb, with the focus at its centre. This was tested by noting the position of the transmitted beam on the wall at the farthest end of the room. Even in extreme cases the maximum deviation of the rays from the axis of the track, as judged by the size of the same projection, was not more than 2° or 3°.

Just at the focus the track in the liquid was found to be practically parallel, and a small length of the track at this portion, limited by a sharp, clean cut rectangular aperture in a thin metal plate attached to the observation side of the tank, was chosen for observation. The imperfection of

polarization of the transversely scattered light was measured
by the usual method due to Cornu, with the help of a double-
image prism and nicol mounted on a stand so as to be capable
of independent rotation about the same axis. The two
images of the track were brought in a line so as *just* to touch
each other. The axis of the prism-nicol combination was
now adjusted so as to be exactly perpendicular to the axis of
the track in the bulb, the two images appearing in the centre
of the field of view. Any slight inaccuracy in this adjust-
ment would not of course, as Rayleigh has pointed out,
appreciably affect the result. Particular care was taken to
cover up the passage of the scattered light from the obser-
vation window to the prism-nicol combination with a black
cloth, so as to avoid any extraneous illumination of the field
of view. The background was quite satisfactory.

Any slight discontinuity in width at the line of contact of
the two images, when they had been brought in a line, which
might arise if the aperture limiting the length of the track
were not exactly in front of the focus, was remedied by
slightly moving either the condensing lens or the aperture.
Otherwise serious error might creep in, since the eye would
compare only the portions of either image immediately
adjoining the line of separation. In order further to guard
against this error, the observations were always repeated
with the double-image prism turned over 180°, and thus with
the position of the strong and weak images interchanged.
But in general there was not any appreciable difference
between the two sets of readings. For each position of the
prism two sets of readings were taken, rotating the nicol in
its mount between the two sets so as to get the readings on
different parts of the scale. For each position of equality
two readings were taken approaching from either side. In
order to minimize the action of light, if any, on the liquid,
the light was kept on only for just the time necessary for
taking observations.

In connexion with the remarks above on the discontinuity
in width of the two images at the line of contact, it might be
supposed that it would be an advantage to use a narrow
parallel beam for the incident light instead of the convergent
beam. However, owing to the converging action of the
spherical bulb of liquid the actual track inside the bulb
would cease to be parallel. An incident divergent beam is
also out of the question, since the actual divergence ought to
be capable of continual variation in order that on entering
the various liquids the tracks inside might be parallel. Of
course, all this trouble can be avoided if we use the same

liquid for the tank as is contained inside the bulb, but this is also not quite practicable when working with a large number of liquids.

In the case of a number of liquids, the imperfection of polarization was measured also for different parts of the spectrum, using for the purpose coloured filters. Where any difference was detected between the values for different portions of the spectrum the liquid was tested for fluorescence, by the method used by Ramanathan *, by transferring the coloured filters from the path of the incident beam to that of the scattered beam and testing whether the value for the imperfection was altered.

For measurements of the relative intensities of the scattered light a telescope objective of about 140 cm. focal length was used to concentrate the rays. The objective was limited, as before, by an aperture 1·4 cm. sq.; the beam emerging out of the telescope was very nearly parallel, and the central portion of this concentrated beam was allowed to pass through another aperture 4 mm. sq. before passing through the bulb. The bulb was immersed as in depolarization measurements in a tank, the liquid used in general in the tank being distilled water. But for liquids having a high refractive index, *i. e.* above 1·5, in order to avoid errors arising from the magnification of the track in the bulb due to its sphericity, a mixture of benzene and carbon disulphide having nearly the same refractive index as the liquid inside the bulb was used.

A block of homogeneous, colourless Jena glass, 2 cm. thick, was chosen as a secondary standard, its scattering being of the same order of magnitude as in most of the liquids and forming a perfect colour match with the same. The glass block, which was completely blackened, excepting for the usual three windows, was placed in the bath in front of the bulb to be compared and closely touching it, the beam of light passing transversely through the place of contact. Two small similar portions of the tracks on either side were selected for comparison, by using two rectangular apertures in a line, with a short opaque portion between them, which served to cut out the light diffused at the surface of contact. The diffusion was unavoidable, so that the two portions of the track compared had to be separated by a few mm. (4 mm.); and due to this separation the comparison was by no means as accurate as in the case of polarization measurements. The comparison was made with the help of an

* *Loc. cit.*

Abney rotating sector photometer. The secondary standard was finally compared with a freshly prepared bulb of ethyl ether

3. *Results.*

In Table I. are given the results of the measurements on the imperfection of polarization of the scattered light with white light and also with coloured filters interposed in the path of the incident and scattered light. The ratio of the weaker component, having its vibrations parallel to the incident beam, to the stronger component having its vibrations perpendicular to the same, is expressed as a percentage. In general, only blue and orange filters were used and occasionally green. Even though red would have been preferable to orange, being at the end of the spectrum, the latter was used owing to the much larger intensity of the light transmitted.

TABLE I.

Depolarization of the Light transversely scattered by the Liquids at 30° C.

White incident light.

Substance.	$\dfrac{\text{Weak component}}{\text{Strong component}} \times 100$	Substance.	$\dfrac{\text{Weak component}}{\text{Strong component}} \times 100$
PARAFFINS AND UNSATURATED FATTY HYDROCARBONS.		CHLORIDES.	
		Propyl chloride	16·3
Pentane	7·8	Isopropyl chloride	16·2
Isopentane	5·6	Isobutyl chloride	16·5
Hexane	9·9	Allyl chloride	36
Heptane	10·0	Methylene chloride (Dichlormethane)	31
Octane	12·9	Ethylene chloride	36
β-isoamylene (Trimethyl Ethylene)	25·8	Chloroform (Trichlormethane)	24·2
BROMIDES.		Carbon tetrachloride (Tetrachlormethane)	6·1
Ethyl bromide	25·0	Silicon tetrachloride	5·8
Propyl bromide	25·0		
Isobutyl bromide	26·4		
Allyl bromide	59		
Ethylene bromide	61		

TABLE I. (*continued*).

Substance.	White light.	Orange filter in the path of		Green filter in the path of		Blue filter in the path of	
		incident light.	scattered light.	incident light.	scattered light.	incident light.	scattered light.
SULPHUR COMPOUNDS.							
Carbon bisulphide	69	68·5	70	...	...	71	73
Methyl sulphide	12·9						
Ethyl sulphide	18·2						
FATTY ACIDS.							
Formic acid	5·,						
Acetic acid	47	47	47	...	...	48	48
Propionic acid	41	41	42	42	41·5	49	47
Butyric acid	40	36	39	41·5	44	68	55
OXIDES (ANHYDRIDES).							
Acetic anhydride	43						
Propionic anhydride ...	44						
Ethyl ether	9·1	8·0	9·3	8·3	8·9	10·9	8·8
BENZENE AND ITS DERIVATIVES.							
Benzene	47	47	47	48	48	50	51
Toluene (Methyl benzene).....	52·5	52·5	52	55 (?)	51	57·5	59
Ethyl benzene	53	54	53	53	55	53	59
Ortho-xylene	40	40	38	...	...	42	41
Meta-xylene	57	56	60	...	...	64	61
Para-xylene	66	66	67	...	...	67	68
Benzyl chloride	58	56	61	...	...	73	54
Benzal chloride	55	52	55	...	...	71	53
Chlorobenzene	58	57·5	58	61 (?)	61 (?)	56	55
Bromobenzene	65						
Nitrobenzene	74						
Aniline	60						
Ortho-nitrotoluene	82						
Meta-nitrotoluene	83						

TABLE I. (*continued*).

Substance.	White light.	Orange filter in the path of		Green filter in the path of		Blue filter in the path of	
		incident light.	scattered light.	incident light.	scattered light.	incident light.	scattered light.
ALCOHOLS.							
Methyl alcohol	8·2	6·0	8·0	...	...	12·6	7·4
Ethyl alcohol	6·8	5·3	7·1	...	...	10·5	6·8
Propyl alcohol	7·6	7·1	9·9	...	...	11·0	7·2
Isopropyl alcohol	7·2	5·0	6·7	...	...	10·7	7·2
Butyl alcohol	11·5	9·3	11·0	...	...	14·9	11·0
Isobutyl alcohol	11·2	7·3	11·8	...	...	16·3	9·0
Tertiary butyl alcohol (Trimethyl carbinol)	6·2	4·1	5·8	...	...	9·2	5·6
Amyl alcohol (inactive)	11·9	9·8	12·5	...	..	27·9	10·8
Allyl alcohol	29·3	29·6	29·4	34	31	38	37
Benzyl alcohol	65	62	63	...	...	67	66
ESTERS.							
Methyl formate	28·1						
Ethyl formate	22·1	21·3	21·6	...	...	20·7	19·6
Propyl formate	21·0	21·0	21·1	18·1	20·4	18·6	17·7
Ethyl acetate	23·3						
Propyl acetate	21·7						
ACETALDEHYDE AND KETONES.							
Acetaldehyde	20·0	18·9	19·4	...	...	21·6	19·0
Dimethyl ketone	23·6						
Methyl ethyl ketone	17·4	16·6	18·1	...	...	25·5	18·2
Diethyl ketone	36	18·0	36	...	...	78	24·9
Methyl propyl ketone	19·6						
Water	9·6	8·5	11·8	7·9	9·5	14·5	9·9

The orange filter, as tested by a direct-vision spectroscope, transmitted the region of the spectrum from greenish yellow to red ; the green filter transmitted, in addition to green, a little blue and a small region at the extreme red ; the blue filter, while transmitting mostly blue and violet, allowed to a more or less extent almost the whole visible region to pass. Thus the light transmitted by the filters extended over large regions. However, since the observations were all visual and the purpose was to test in a general way the influence of the frequency of the incident vibrations on the depolarization, homogeneity was not considered necessary.

In Table II. the observed intensities with white incident light are given in terms of the light scattered by ethyl ether. Ether was chosen for comparison since its intensity is of the proper magnitude and the liquid is easily got pure and is not acted on by light. The figures in the table give the actual values obtained by experiment, no correction having been made either for absorption or for reflexion at the various surfaces. For the small distances involved, the absorption, even when not wholly accounted for by scattering, would be quite negligible. As for the reflexions, in the case of the track in the liquid, 2 water-glass and 2 glass-liquid surfaces had to be taken into account more than in the case of the track in glass, and since the incidences were normal, a little calculation shows that, even in extreme cases, the loss would not be appreciable.

In the case of nitro-benzene and nitro-toluene, which were coloured greenish yellow, a filter of about the same colour was used in the path of the incident light.

4. *Discussion of Results.*

(i.) *Feeble fluorescence and its influence on the polarization of the scattered light.*

In some of the liquids given above, the imperfection is affected by transferring the coloured filter from the path of the incident beam to that of the scattered beam. This may be considered as a very feeble kind of fluorescence. To see how this would influence the polarization, let us, for example, consider the case where the blue region of the spectrum excites a fluorescence which lies mainly in the green. With the blue filter in the path of the incident beam, the scattered light would be mixed up with the fluorescent light, and if we assume, as we may reasonably, that the fluorescent light is mostly unpolarized, the light observed would show an abnormal imperfection of polarization. On transferring the

TABLE II.—Intensity of the transversely scattered Light.

Substance.	r.	n_F.	$\beta \times 10^8$ per atm.	Intensity at 30° C. (Ether=1).			Remarks.
				Calculated.	Observed.	Values obtained by other investigators.	
Pentane	·078	1·353	235	1·12	1·14		
Isopentane	·056	1·352	238	1·06	1·06		
Hexane	·099	1·374	169	0·99	1·00		
Heptane	·100	1·387	142	0·92	1·00	1·13 at 18°C. (M.L.)	
Octane	·129	1·396	128	0·94	0·96		
β-isoamylene	·258	1·381	199	1·78	1·54		
Ethyl bromide	·250	1·423	144	1·71	1·58		
Allyl bromide	...	...	...	...	3·10		
Ethylene bromide	...	...	...	...	3·42		
n-Propyl chloride	...	...	...	...	1·34		Background not satisfactory owing to white deposit on the sides of the bulb.
Isopropyl chloride	...	...	...	...	1·38	...	
Allyl chloride	...	...	...	...	1·47		
Methylene chloride	·36	...	...	...	1·24		
Ethylene chloride	...	1·445	87	1·60	1·44		
Chloroform	·242	1·446	110	1·50	1·26		
Carbon tetrachloride	·061	1·462	114	1·14	1·02		
Silicon tetrachloride	...	...	...	...	1·13		
Carbon bisulphide	·685	1·642	101	21·3	13·0	18·6 (R.R.) 12·8 (M L.)	
Methyl sulphide	...	...	...	...	1·22		
Ethyl sulphide	...	...	...	...	1·33		
Formic acid	...	...	...	...	1·22		
Acetic acid	·47	1·373	98·5	1·50	1·19		
Propionic acid	...	...	...	...	1·24		
Butyric acid	...	...	...	...	1·19		
Acetic anhydride	...	...	...	...	1·01	......	Liquid left over after distillation distinctly coloured, indicating decomposition.
Propionic anhydride	...	...	...	...	1·41		

Substance		n_D					Remarks
Benzene	·47	1·507	103	3·90	3·15	3·64 (R.R.) 2·82 (M.L.) 3·45 (R.R.) 3·21 (M.L.)	Calculated values not quite reliable since a small error in r makes a large difference. Aniline not quite free from dust particles.
Toluene	·525	1·501	97	4·28	3·53		
Ethyl benzene	·53	1·502	92	4·17	3·18		
Meta-xylene	·57	1·502	91	4·82	3·87		
Para-xylene	·66	1·501	94	7·61	4·61		
Benzyl chloride	...	...	...	...	3·50		
Benzal chloride	...	...	...	...	3·21		
Chlorobenzene	·58	1·531	80	5·27	4·10		Ortho-nitrotoluene contains a number of dust particles and its intensity was calculated for 14° C. from the values of n and $\dfrac{\partial n}{\partial p}$.
Bromobenzene	·65	1·568	72	8·21	4·92	4·11 (M.L.)	
Nitrobenzene	·74	$n_D = 1·548$	53	10·0	10·5		
Aniline	·60	1·599	48	5·18	3·42		
Ortho-nitrotoluene	·82	...	...	29	9·40		
Meta-nitrotoluene	...	...	...	...	9·80		
Methyl alcohol	·060	1·329	131	0·49	0·78?	·58 (R.R.) ·54 (M.L.)	Liquid left over after distillation is coloured dark brown.
Ethyl alcohol	·053	1·363	121	0·59	0·58	·72 (R.R.) ·56 (M.L.) 0·73 (M.L.)	† A yellow filter was used in the path of the incident light in working with Benzyl and Benzal chlorides.
n-Propyl alcohol	·071	1·385	105	0·63	0·62		
Isopropyl alcohol	·050	1·380	112	0·62	0·60		
n-Butyl alcohol	·093	1·400	97	0·68	0·65		
Isobutyl alcohol	·073	1·397	105	0·69	0·74	0·79 (M.L.)	
Trimethyl carbinol	·041	1·388	120	0·69	0·69		
Amyl alcohol (inactive)	·098	1·408	110	0·82	0·74		
Allyl alcohol	·296	1·419	100	1·29	1·22	0·84 (M.L.)	
Benzyl alcohol	·62	1·547	60	5·20	2·93		
Methyl formate	...	...	...	...	1·09		Not quite dust-free.
Ethyl formate	·210	1·379	120	0·94	1·00		
Propyl formate	·233	1·372	125	0·98	0·94		
Ethyl acetate	...	...	...	...	0·98		
Propyl acetate	...	...	...	...	0·95		
Acetaldehyde	...	...	...	...	0·89		
Dimethyl ketone	·236	1·358	130	0·92	0·81		Show a tendency to decomposition.
Methyl ethyl ketone	...	...	...	...	0·80		
Diethyl ketone	·18	1·392	110	0·88	1·06		
Water...	·085	1·336	45	0·19	0·21	0·19 (M.L.) 0·19 (R.R.)	

R.R. Ramen and Rao *loc. cit.*   M.L. Martin and Lehrman *loc. cit.*

blue filter to the path of the scattered beam, however, the imperfection would become normal. If, instead of a blue filter, we use a green filter, normal polarization would be observed when the filter is in the path of the incident beam, and an abnormally high polarization when in the path of the scattered beam.

Of the liquids investigated, water, ether, all the mono-hydric alcohols, benzyl and benzal chlorides, methyl ethyl ketone, diethyl ketone, and to a slight extent butyric acid and acetaldehyde, exhibit a feeble fluorescence. From a comparison of the values for the two positions of the filter it is evident that in all the cases mentioned above, the exciting region is at the blue end of the spectrum, the excited region coming much lower down, including to an appreciable extent the orange.

Now, since the orange is in the excited region far removed from the exciting region, on the longer wave-length side, we may safely assume that the value for the ratio of the components obtained with orange incident light is the normal value, there being no question of fluorescence here. Comparing with this value the value with the blue filter in the path of scattered light, we find the latter is generally the higher, leading to either of the following two conclusions :—
(1) The exciting region extends higher up the spectrum than the blue, say to the violet, so that a part of the fluorescent light due to the violet is in the blue, of course without prejudice to the exciting power of blue itself. (2) The normal value of the depolarization for blue light is itself greater than the value for orange. The latter seems to be more probable.

It must be pointed out here that the above liquids are not fluorescent to anything like the same extent as what are usually known as fluorescent substances. Except in the case of a few liquids, practically no difference of colour was noticeable between the two images of the track while using blue incident light, which shows that the amount of light fluoresced is only a small fraction of the scattered light ; and when we remember that the scattered light per unit volume is of the order of 10^{-4} to 10^{-5} of the incident light, we can have an idea of the magnitude of the effect. In fact, it is theoretically possible to calculate the ratio of the intensity of the fluoresced light in a direction transverse to the incident beam to the light scattered in the same direction, *provided we assume that fluorescence is entirely independent of scattering and is a superposed phenomenon.* Thus, taking for example the case

of ether, the ratio $= \dfrac{2\theta}{108\cdot8}$, where $\dfrac{8\cdot8 + \theta}{100 + \theta} = \dfrac{10\cdot9}{100}$, *i. e.* 4 per cent. In the case of methyl alcohol it is about 10 per cent., while with amyl alcohol it is about 40 per cent., and with benzal chloride as high as 80 per cent.

It is significant that, among the liquids examined, those which show this type of fluorescence have a certain family relationship : thus the list includes water and all the monohydric alcohols which have the OH radicle in common, acetaldehyde and the two ketones which have the CO radicle in common, and the fatty acids having the COOH radicle, and benzyl and benzal chlorides. They are also, in general, liquids whose molecules are known to be polar.

(ii.) *Influence of wave-length.*

Coming next to the question of the effect of wave-length on the depolarization, we have already pointed out that among the fluorescent substances, the normal value for the blue might be greater than the normal value for the orange ; and this seems to be particularly true of butyric and propionic acids. Among the non-fluorescent liquids, allyl alcohol, and to a less marked extent benzene, toluene, ethyl benzene, and benzyl alcohol seem to show a similar increase as we proceed from orange to blue.

(iii.) *Relation between depolarization and chemical constitution.*

We may take for consideration the values obtained with orange incident light in the case of liquids which have been examined with coloured filters, and with white light in other cases. Of course, for a proper discussion of the relation between the optical anisotropy of the molecule and its constitution, we must proceed on data for the gaseous state. However, there are certain prominent features which might well be pointed out here.

One principal point that strikes us at the outset is that optical anisotropy does not always go hand in hand with the asymmetry of shape of the molecule. For example, the long chain compounds of the paraffin series show much smaller imperfection of polarization than the ring compound benzene. But within the same series of compounds, increased symmetry causes more perfect polarization. This is well illustrated by the normal and iso-compounds of the paraffin series, by the three isomerides of butyl alcohol, and by the three chlorine substitution products of methane, CH_2Cl_2, $CHCl_3$, and CCl_4. The last case is of particular interest, as with the accepted

structure of the compound with tetrahedral symmetry, we
might expect the scattered light to be completely polarized.
The actual value obtained (6·1 per cent.), though much
smaller than the earlier value of Raman and Rao, is still too
large to be attributed to experimental error. In the case of
$SiCl_4$ the ratio is of the same order, namely 5·8 per cent.*

In a strictly homologous series of paraffins and alcohols,
the depolarization generally increases as we go up the series,
while, in the fatty acids, anhydrides and esters, the value
decreases. The effect of the unsaturation of carbon on the
anisotropy of the molecule is quite marked, the value for the
unsaturated compounds being much higher than that for
the corresponding saturated compounds, as is clear from
Table III. given below.

TABLE III.

Unsaturated.	r (per cent.).	Saturated.	r (per cent.).
β-iso amylene	25·8	Isopentane	5·6
Allyl bromide	59	Propyl bromide ...	25·0
Allyl chloride	36	Propyl chloride ...	16·3
Allyl alcohol	29·6	Propyl alcohol	7·1

When we come to the aromatic compounds, the most
striking feature is the very large value for the depolariza-
tion characteristic of all of them, the value in certain cases
approaching the limit ($\frac{6}{7} = 86$ per cent.), showing that the
" density scattering " in these cases is small in comparison
with " orientation scattering." The values for the three
isomeric xylenes may be pointed out here as illustrating the
marked influence of the relative positions of the side chains
on the anisotropy of the molecule.

(iv.) *Intensity of the scattered light.*

In column 5 of Table II. are given the intensities of the
transversely scattered light calculated from the Einstein-
Smoluchowski formula, with the correction factor for im-
perfect polarization already mentioned (equation (1)), and in

* A redetermination of the ratio for CCl_4 vapour has been recently
made in this laboratory by Mr. A. S. Ganesan, who has obtained the
value 1·8 per cent. A similar determination for SiCl vapour and for
CH_4 would be of interest.

column 6 the observed intensities. Both are expressed as ratios referred to transverse scattering by ethyl ether as unit. Columns 2, 3, and 4 give the values of r, n, and β respectively used in the calculation. For reasons given at length by Ramanathan in an addendum to a recent paper [*], the refractive indices (n) of the liquids for the F line have been adopted for calculation. They were taken from Landolt-Börnstein Tables (1923) and reduced to the temperature of the experiment, viz. 30° C., by using the Lorentz-Mosotti formula and the known constants of thermal expansion. In a few cases where direct experimental data for the refractive index were not available, the values have been calculated from the atomic refractivities.

The most reliable data we have regarding the isothermal compressibilities of liquids for *30° C. and 1 atm. press.* are those of Tyrer [†]. He has experimentally determined the adiabatic compressibilities at different temperatures, for the range 1–2 atm., and from thence calculated the isothermal compressibilities. However, the other investigators, excepting Gay [‡], have determined the isothermal compressibilities directly, and since, as has been pointed out by Tyrer, it is extremely difficult to eliminate the heat of compression while working with small ranges of pressure changes, the direct measurements by the majority of investigators at low pressures give values somewhere between the isothermal and adiabatic compressibilities. Naturally the values obtained by the different investigators do not agree among themselves.

The values of Tyrer have been adopted wherever available, in other cases the values of other investigators (taken from 'Piezochemie' by Cohen and Schut) have been used, the closeness of the agreement between their values and those of Tyrer, where they are both available, being used as a criterion for choosing from among them. In this respect the values obtained by Röntgen [§] (1–8 atms. and at 3° C.– 6° C. and about 18° C.), when extrapolated to 30° C., agree best with Tyrer's. In some liquids which have been investigated only at high pressures the values for 1 atm. had to be extrapolated from the scanty data at higher pressures.

Before preceeding to compare the calculated and observed values of the intensity, there is one other point regarding the calculation, pointed out to the writer by Prof. Raman, which

[*] Phys. Rev. xxi. p. 564 (1923).
[†] Journ. Chem. Soc. London, cv. p. 2534 (1914).
[‡] *Comptes Rendus*, clvi. p. 1979 (1913).
[§] *Wied. Ann.* xliv. p. 1 (1891).

must be mentioned here. The original expression obtained by Einstein for the fraction of the incident light scattered transversely per unit volume per unit solid angle was

$$I_1 = \frac{2\pi^2 RT}{N\lambda^4} \cdot \frac{n^2\left(\dfrac{\partial n}{\partial p}\right)^2}{\beta} \quad . \quad . \quad . \quad . \quad (2)$$

Now $\dfrac{\partial n}{\partial p}$ has been measured directly by experiment for some liquids by Röntgen and Zehnder * and recently by Himstedt and Wertheimer †, and Eisele ‡, and might be used in the calculation. But since the number of liquids for which such data are available is small, the value of $\dfrac{\partial n}{\partial p}$ given by the Lorentz-Mosotti relation has been used in all cases for the sake of uniformity, thus getting the Einstein formula in the usual form,

$$I_2 = \frac{\pi^2 RT\beta}{18N\lambda^4} (n^2-1)^2(n^2+2)^2. \quad . \quad . \quad (3)$$

However, we can get a general idea of the error involved in such a substitution by seeing how nearly $\dfrac{I_1}{I_2}$ for the F line and 30° C. is equal to unity. No direct data are available for calculating $\dfrac{\partial n}{\partial p}$ and thence $\dfrac{I_1}{I_2}$ *for the* F *line and 30° C.* But a calculation of the values of the ratio $\dfrac{I_1}{I_2}$ for different wave-lengths from the experimental values of $\dfrac{\partial n}{\partial p}$ obtained by Himstedt and Wertheimer and Eisele, and for different temperatures from the values obtained by Röntgen and Zehnder, shows that the variation of $\dfrac{I_1}{I_2}$, if any, with wave-length or temperature is very small. We may therefore take those values (given in column 3 of Table IV.) as applying equally well for the F line and 30° C. Column 4 of the same table gives those values relative to ether, and they are obviously the correction factors to be applied on this account to the calculated values of the intensity relative to ether in column 5 of Table II.

* *Wied. Ann.* xliv. p. 22 (1891).
† *Ann. der Phys.* lxvii. p. 395 (1922).
‡ *Ann. der Phys.* lxxvi. p. 396 (1925).

TABLE IV.

	Liquid.	I_1/I_2 for the liquid.	$\dfrac{I_1/I_2 \text{ for the liquid.}}{I_1/I_2 \text{ for ether.}}$
1.	Water	·79	·91
2.	Hexane	·97 (?)	1·12
3.	Chloroform	·90	1·04
4.	Carbon bisulphide	·80₅	·93
5.	Benzene	·80₅	·93
6.	Toluene.......................	·80	·92
7.	Ethyl benzene	·73	·84
8.	Chlorobenzene	·82	·95
9.	Bromobenzene	·75	·87
10.	Nitrobenzene	·81	·94
11.	Methyl alcohol	·89	1·03
12.	Ethyl alcohol	·87	1·01
13.	Propyl alcohol..............	·87	1·01
14.	Isopropyl alcohol	·89	1·03
15.	Butyl alcohol	·89	1·03
16.	Isobutyl alcohol	·90	1·04
17.	Benzyl alcohol..............	·63	73
18.	Dimethyl ketone	·85	·98
19.	Ethyl ether	·86₅	1·00

Thus, even though the absolute values of the intensity calculated by the two methods, viz. eqns. (2) and (3), widely disagree, the correction factors for the values relative to ether except in the case of liquids with high ref. index, water and hexane are very nearly equal to unity.

Now, coming to the actual comparison of the observed and calculated values of the intensity of the transversely scattered light, we find that in a large number of liquids the agreement is all that could be desired, especially when we consider the experimental imperfections and the uncertainties in the values of β used in the calculation. In a few of the other liquids the discrepancy might probably be explained away. Thus in the case of β-isoamylene and ethyl bromide the difference might be neglected. And with acetic acid it might be due to the presence of water, since it shows a strong tendency to adsorb it and, as already mentioned, no special precautions were taken to dry the liquids. However, data for calculating the values for the other fatty acids and

anhydrides might help us in settling this point. Diethyl ketone is so strongly fluorescent that the track with white light shows a distinct greenish tinge. Hence the larger observed value might be due to the contribution from fluorescence, since white incident light was used for intensity measurements. Dimethyl ketone is probably fluorescent like the other two ketones examined, in which case, the white light value for r used in the calculation would certainly be too high, and that would explain the higher calculated value. Further, the ketones show a strong tendency to decomposition.

With ethylene chloride, chloroform, and carbon tetrachloride the observed values are definitely smaller than the calculated values, and they might be classed along with the liquids to be mentioned below. But the discrepancy in these cases is not sufficiently large to justify any conclusion based on them.

Thus even in the above liquids, we cannot say definitely that there is disagreement with theory.

However, we are still left with CS_2 and all the aromatic compounds (even nitrobenzene is probably no exception) where, as a rule, the observed values in terms of ether as a standard are much smaller than the calculated values, even taking into account the correction already mentioned for the value of $\dfrac{\partial n}{\partial \rho}$ used in the calculation. Here the theoretical expressions for the intensity seem definitely to break down.

5. *Summary.*

1. The paper describes measurements of the intensity and the imperfection of polarization for different regions of the spectrum, of the light scattered transversely by 65 different dust-free liquids, mostly carbon compounds.

2. It is found that some of the liquids are feebly fluorescent, the blue end of the spectrum, in general, exciting fluorescence, the fluorescent light being in the less refrangible region. An estimate is made of the magnitude of this effect.

3. In some of the liquids there seems to be a genuine dependence on wave-length of the depolarization ; the imperfection of polarization increases as the wave-length diminishes.

4. Some prominent features of the relation between the depolarization and chemical constitution are pointed out.

5. The theoretical formula for the intensity is found to

fail in the case of high refractive index liquids (which are also, in general, liquids which show a high depolarization).

In conclusion, the writer has great pleasure in expressing his indebtedness to Prof. C. V. Raman for his kind interest in the work. The experiments were for the most part carried out in the spring and summer of 1924, in the Physical Laboratory of the Indian Association for the Cultivation of Science.

210 Bowbazaar Street,
    Calcutta, India.
        April 16, 1925.

LXXVI. *Note to "Refraction and Electron Constraint in Ions and Molecules"* *. *By* Charles P. Smyth, *Department of Chemistry, Princeton University, Princeton, N.J., U.S.A.*†

A METHOD similar to that which I have employed for calculating the refractions of electron groups was proposed by K. Fajans and C. A. Knorr in a communication to the Bunsengesellschaft ‡, which had escaped my attention. Two months after the correction and dispatch of the proof, but before the actual publication of my paper, " Refraction and Electron Constraint in Ions and Molecules," I was enabled by Professor Fajans to examine the manuscript of an unpublished dissertation by Dr. Knorr, in which this method was applied and a large number of results obtained identical with those appearing in my paper. Although the work of Professor Fajans and Dr. Knorr, which will be published shortly, does not cover precisely the same ground as that covered by my paper and although differences in the details of interpretation are apparent, their work, done quite independently, may be regarded as agreeing substantially with mine.

Munich, Germany.
    July 30, 1925.

LXXVII. *Variation of Logarithmic Decrement with Amplitude and Viscosity of Certain Metals.*—II. *By* G. Subrahmaniam, *M.A., A.Inst.P.**

IN a former communication to the Philosophical Magazine †
the authors have studied at some length the variation of
logarithmic decrement with amplitude and viscosity of three
materials : copper, brass, and steel. The present paper is a
continuation of the same investigation, and deals with the
behaviour of wires made of five more solids—namely, of pure
specimens of the metals aluminium and iron, and of the
alloys eureka (constantan), manganin, and german silver.
These alloys are labelled as having the composition : 60Cu,
40Ni; 84Cu, 12Mn, 4Ni; and 60Cu, 15Ni, 25Zn respectively.

As has been stated already, the behaviour of wires is
influenced to a marked extent by (1) internal friction and
(2) elastic fatigue or after-effect. The results of these
experiments seem to confirm the view that the viscous resistances called into play when a wire is set in vibration, and
to which the decay is largely due, are not of the ordinary type,
that is to say, such as are proportional to the rates of strain.

The experimental arrangements are quite similar to those
already described in detail in the former communication.
Each of the test-wires is subjected to a preliminary treatment before experimental observations are made. It is kept
stretched by half the maximum load which it can carry for
the given dimensions, and is allowed to remain in that state
for a few days. The wire is then arranged in the air-free
chamber, and is set in a state of torsional vibration through
a small angle. As in the previous experiments, the logarithmic decrement for *a given amplitude* is found to fall off
progressively in the initial stages, so that no two consecutive
sets of readings agree closely. It is therefore found necessary
to keep the wires in a state of continuous vibration for indeed
a very long time before perfect consistency can be achieved.
The interval is different for different metals. This is evidently the result of the elastic after-effect, as has been
clearly recognized by Streint ‡, Kei Iokibe and Sukeaki
Sakai §, and others engaged in similar investigations. The
view put forward by Thomson ‖ that the logarithmic decrement is uninfluenced by such treatment seems, therefore, to be
untenable.

* Communicated by Prof. E. H. Barton, D.Sc., F.R.S.
† G. Subrahmaniam and D. Gunniaya, Phil. Mag. April 1925, p. 711.
‡ *Sitzb. der Wien. Akad.* vol. lxix. Abth. 2, p. 237 (1874); lxxx.
Abth. 2, p. 387 (1880).
§ Phil. Mag. Sept. 1921, pp. 397–418.
‖ Phys. Rev. vol. viii. p. 141 (1889).

The results of these experiments are plotted on graph paper. As the curves indicate the readings sufficiently accurately, tables of values are omitted from the paper.

A STUDY OF THE RESULTS.

In all these experiments the scale is, as usual, kept at a constant distance of 74 cm. so that an amplitude of 1 cm. is equivalent to a twist of $\frac{1}{74 \times 2} \times \frac{180}{\pi} = 0.39$ of a degree. As the deflexion never exceeds about 14 cm., the maximum angular twist to which each of the test-wires is subjected is about $5°$.

(1) *Aluminium Wires* (Graphs I. & II.).

Graph I.—Aluminium Wire (diam. 0·105 cm.).
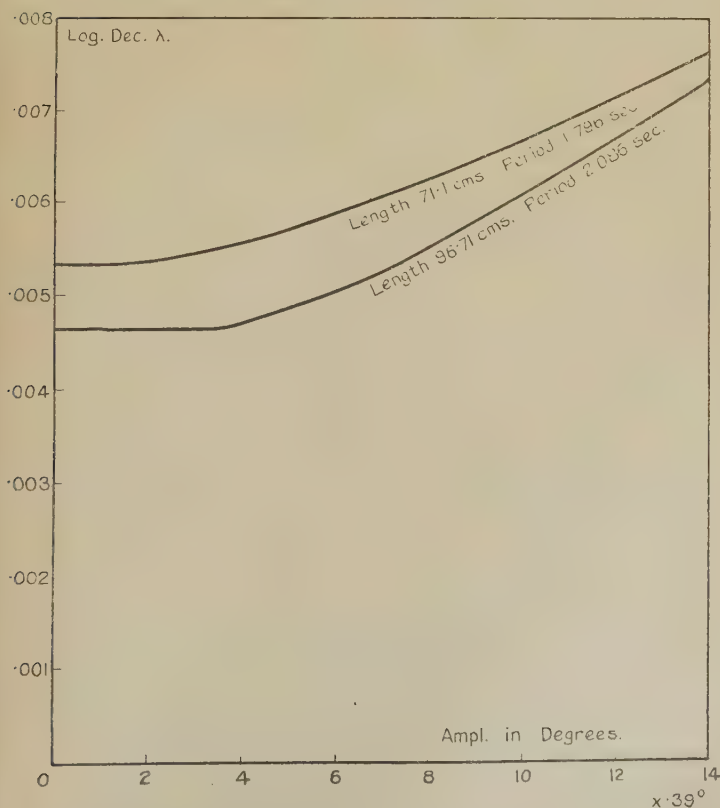
Two different thicknesses of aluminium wire are used. With the thicker wire (diam. 0·105 cm.), length 96·71 cm.,

the decrement has a constant value of 0·004624 until the twist per unit length reaches 0·68 of a minute. Thereafter it is found to increase linearly with amplitude. As the angular amplitude is increased to about 5°, which, as has been mentioned already, is the maximum twist used in these experiments, the logarithmic decrement increases to about ·007308, *i.e.* by 58 per cent. of its constant value. When

Graph II.—Aluminium Wire (diam. 0·073 cm.).
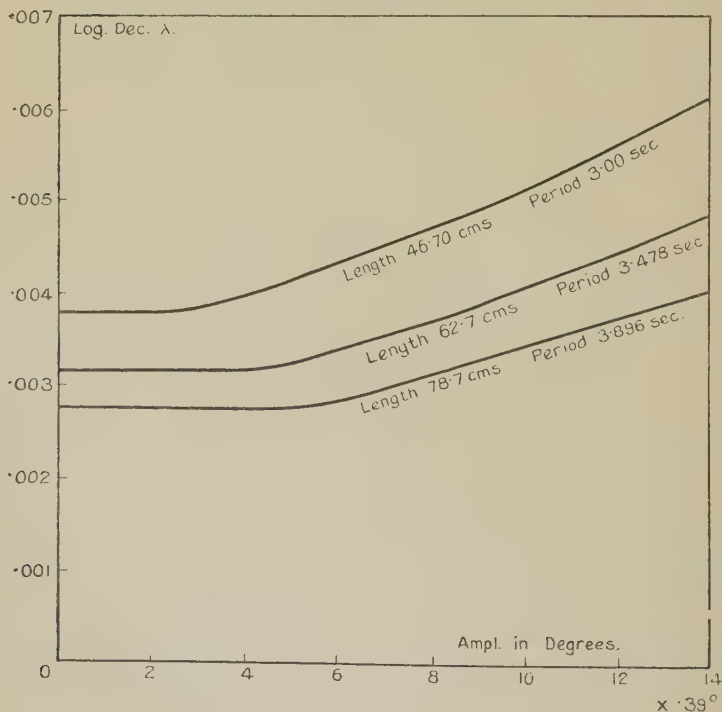
the length of this wire is made 71·1 cm., the decrement has a constant value of ·005330 so long as the twist per unit length does not exceed ·54'. For greater twists the decrement varies directly with the amplitude. As the total twist of the wire is increased to about 5°, this value rises to ·007708, *i.e.* by 45 per cent.

With the thinner wire (diam. 0·073 cm.), length 78·7 cm., the decrement remains constant at ·002742, and is found to increase when the twist exceeds about 1'·4 per cm. As the

total twist is increased to the maximum extent, the decrement rises to 004081, *i. e.* by 49 per cent. With lengths 62·7 and 46·7 cm. of the same wire the decrement is observed to be constant at ·003147 and ·003783, corresponding to limiting twists of 1′·5 and 1′·3 per unit length respectively. For the maximum twist the decrements are found to increase by 56 per cent. and 63 per cent.

(2) *Iron Wire* (Graph III.).

The general form of the curves is identical with those for aluminium. When the length of the test-wire is 38·3 cm., the decrement is steady at ·001070 for twists below 4′·3 per cm. As the twist is further increased, the decrement

Graph III.—Iron Wire (diam. 0·0228 cm.).
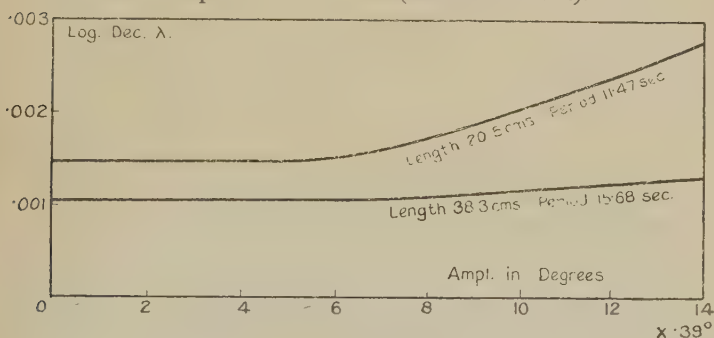
increases proportionately with amplitude, and the maximum value observed is about 25 per cent. greater. With the shorter length of the wire, *i. e.* 20·5 cm., the decrement remains constant at ·001488 until the twist per unit length amounts to 5′·9. Thereafter it rises to 002792, *i. e.* by 86 per cent. as the total twist approaches 5°.

(3) *Eureka or Constantan Wire* (Graph IV.).

Graph IV.—Eureka Wire (diam. 0·071 cm.).
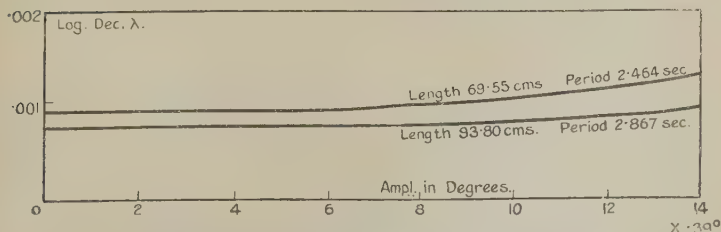
In the case of the constantan wire, length 93·8 cm., the decrement is ·0007967, and is found to be constant so long

as the twist does not exceed $2'\cdot4$ per cm. For greater twists it proportionately increases, and the decrement for the maximum twist is about 19 per cent. higher. With the shorter length, $69\cdot55$ cm., the decrement is $\cdot0009452$ for values of twist below $2'\cdot6$ per unit length. The maximum observed is 35 per cent. higher.

(4) *Manganin Wire* (Graph V.).

The curve is nearly a straight line parallel to the x-axis for the single length and cross-section used. Owing to an accident during the experiment, the wire happened to be

Graph V.—Manganin Wire (diam. $0\cdot0710$ cm.).
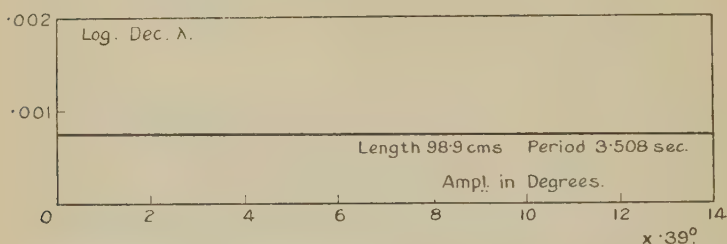
distorted on completion of the first set of observations. I was therefore obliged to be content with readings for a single length. Presumably the curves follow the same course for shorter lengths.

In all the above cases the curves suggest an equation of the form

$$\lambda_a = \lambda_0 + f(a - m),$$

where the constants a and m have different values for different materials. Even for the same metal they are found to vary with the length and thickness. From the values set out in detail it is evident that the curves get steeper as the cross-section and the length are made smaller. This is clearly due to the dissipation of energy.

(5) *German Silver Wire* (Graph VI.).

The curves for german silver wire, on the other hand, are different from those of the other solids examined in this paper. The decrement does not tend to a constant value, but decreases with decreasing amplitude more or less linearly so that

$$\lambda_a = \lambda_0 + f(a).$$

The decrements extrapolated for zero amplitude are ·001537 and ·002016 when the lengths of the wire are 48·95 and 29·3 cm. respectively.

Graph VI.—German Silver Wire (diam. 0·031 cm.).
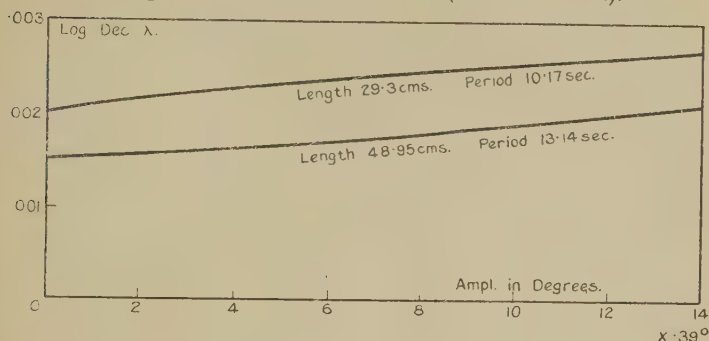
VISCOSITY OF METALS.

With the help of readings so obtained, coefficients of viscosity of different materials have been calculated. In view of the fact that no complete list is available on this point, such a determination will, however, be of some use. Even among the results available there is wide disparity; for instance, Barus [*] obtained for the absolute viscosity of steel an enormously large value, $6{-}60 \times 10^{17}$, while Voigt [†] got $5·48 \times 10^7$ for copper and $4·73 \times 10^8$ for nickel. Kei Iokibe and Sukeaki Sakai [‡], as a result of their experiments with about a dozen metallic elements, obtained values of the order of 10^8. Since the value of the logarithmic decrement of wires varies greatly with the previous history and the conditions under which the measurement is made, coincidence of the values obtained by different investigators is hardly to be expected. But such determinations are calculated to give us the correct order of magnitude of the coefficient of viscosity.

In the following tabular form the minimum values of λ are substituted in the equation $\eta = \dfrac{8I \cdot l\lambda}{\pi \cdot T \cdot R^4}$.

[*] Phil. Mag. (5) **xxix.** p. 337 (1890).
[†] *Wied. Ann.* xlvii. p. 671 (1892).
[‡] *Loc. cit.*

$I = 3563{\cdot}02$ grm. cm.^{2} Temp. $28°{-}31°$ C

Material.	R cm.	l cm.	T sec.	λ.	$\eta = \dfrac{8I l \lambda}{\pi T R^4}$ dynes per sq. cm.
Aluminium	0·0525	96·71	2·086	0 004624	$2{\cdot}558 \times 10^8$
,, ...	,,	71·1	1·796	·005330	$2{\cdot}519 \times 10^8$
,, ...	·0365	78·7	3·896	·002742	$2{\cdot}831 \times 10^8$
,, ...	,,	62 7	3·478	·003147	$2{\cdot}900 \times 10^8$
,, ...	,,	46·7	3·00	·003783	$3{\cdot}009 \times 10^8$
Iron	·0114	38·3	15·68	·001070	$14{\cdot}04 \ \times 10^8$
,, ...	,,	20·5	11·47	·001488	$14 29 \ \times 10^8$
Eureka	·0355	93·8	2·867	·0007967	$1{\cdot}489 \times 10^8$
,, ...	,,	69·55	2·464	·0009452	$1{\cdot}524 \times 10^8$
Manganin	·0355	98·9	3·508	·0007326	$1{\cdot}101 \times 10^8$
German silver	·0155	48·95	13·14	·001537	$9{\cdot}001 \times 10^8$
,, ,, ...	,,	29·3	10·17	·002016	$9{\cdot}133 \times 10^8$

SUMMARY.

(1) Logarithmic decrement and amplitude curves have been constructed for aluminium, iron, eureka (constantan), manganin, and german silver.

(2) In the case of the first three solids the decrement remains constant over a certain range and then increases linearly. For manganin the value is found to be constant within the amplitude used.

(3) The logarithmic decrement for wires made of german silver does not tend to any constant value, but falls off steadily for decreasing amplitudes.

(4) Viscosities of these materials are found to be : aluminium $2{\cdot}763 \times 10^8$, iron $14{\cdot}16 \times 10^8$, eureka $1{\cdot}506 \times 10^8$, manganin $1{\cdot}101 \times 10^8$, and german silver $9{\cdot}067 \times 10^8$ dynes per sq. cm.

In conclusion, the author wishes to thank Prof. E. H. Barton and Prof. A. L. Narayan for their continued interest in this work.

Vizianagaram, S. India,
    May 1, 1925.

LXXVIII. *Note on the Theory of Interionic Attraction in Strong Electrolytes.* By S. R. PIKE, *B.A.*, *and* G. NONHEBEL, *B.A.*, *Scholars of Balliol College, Oxford* *.

IT is now a generally accepted theory that the anomalous behaviour of strong electrolytes in solution is accounted for by the electrical energy of a mixture of dissociated ions. Two calculations of the magnitude of this effect have been published by Milner † and by Debye and Hückel ‡ respectively, and these are unfortunately not in agreement, so that it becomes important to try to distinguish between them.

The earlier calculation, by Milner, gives for the mutual potential energy of a mixture of uni-univalent ions per unit volume :

$$U_e = R\,T\,hf(h), \quad h = \left(\frac{8\pi}{3}n\right)^{\frac{1}{3}}\frac{\epsilon^2}{D\,k\mathrm{T}}, \quad . \quad . \quad . \quad (1)$$

where $2n$ = number of ions per unit volume,

k = gas constant per molecule,

D = dielectric constant of the solvent,

ϵ = charge on an ion,

and $f(h)$ is a tabulated function whose values are not known with any great accuracy.

Debye and Hückel, on the other hand, derive the expression :

$$\left.\begin{aligned}U_e &= \frac{n\epsilon^2\kappa}{D}\cdot\frac{1}{1+\kappa a}\\[2mm]\kappa^2 &= \frac{8\pi\epsilon^2}{Dk\mathrm{T}}\cdot n\end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

and a is an arbitrary ionic radius.

These formulæ do not agree even at extreme dilution for (1) becomes in the limit

$$U_e = n^{3/2}\frac{\epsilon^2}{D}\sqrt{\frac{4\pi^2\epsilon^2}{Dk\mathrm{T}}},$$

whilst (2) becomes

$$U_e = n^{3/2} \frac{\epsilon^2}{D} \sqrt{\sqrt{\frac{8\pi\epsilon^2}{DkT}}},$$

which differ by the factor $\sqrt{\frac{\pi}{2}}$.

The authors then proceed to calculate various "osmotic" quantities, such as freezing-point depressions, activity coefficients, etc., on the basis of their respective values for U_e; and it is usually assumed without further consideration that the two theories may be tested directly by comparing these calculated osmotic quantities with experiment. The object of the present note is to point out the doubtful character of this assumption, and to indicate the most effective method of deciding between results (1) and (2) by appeal to experiment. It will be shown that the thermodynamical conditions to be satisfied in the deduction of these experimental quantities from U_e are such as to make their theoretical values, in part at least, illusory.

Debye and Hückel, following Planck's [*] treatment, derive for the function Φ where

$$\Phi = S - (U + \rho V)/T \quad . \quad . \quad . \quad . \quad (3)$$

for a solution of uni-univalent strong electrolyte the expression

$$\Phi = n_0(\phi_0 - k \log c_0) + 2n(\phi - k \log c) + \frac{2n\epsilon^2}{3DT}\kappa\chi \quad . \quad (4)$$

for unit volume, where

$$\chi = 1 - \frac{3}{4} \ a\kappa \text{ approx.}, \ c = \frac{n}{n_t}, \ c_0 = \frac{n_0}{n_t},$$

the suffix 0 referring to solvent molecules.

Now a purely thermodynamical treatment of the internal energy of a solution has been given by Cavanagh [†], also following Planck, and extending his treatment to the case of less dilute solutions, on the basis of certain very general assumptions. For a solution of a single salt, completely dissociated, these assumptions may be written in the form

$$U = n_0 u_0 + 2nu + n_t \Sigma u_1 f_1(c), \quad . \quad . \quad . \quad (5)$$

where the f's are functions of the concentration only, and the u's are dependent on temperature and pressure only.

* Planck, *Thermodynamik*, 7e Aufl. p. 229.
† Phil. Mag. xliii. p. 606 (1922).

Similar quantities v_1 etc. in the total volume expression may be treated as negligible (D. & H., *loc. cit.* p. 188).

From this we have

$$\Phi = n_0(\phi_0 - k \log c_0) + 2n(\phi - k \log c) + n_t \Sigma \phi_1 f_1, \quad . \quad (6)$$

where the ϕ's obey the equation

$$\phi_1 = K - \frac{u_1}{T} + \int \frac{du_1}{T}, \text{ or } \frac{\partial \phi_1}{\partial T} = \frac{u_1}{T^2}. \quad . \quad . \quad (7)$$

This latter equation must hold good over the entire range of an imaginary process, conceived for the purpose of determining the integration constants, by which the solution is transformed to a mixture of perfect gases. (As regards the validity of this conception, *v.* Planck, *loc. cit.* p. 234.)

Comparing this expression for Φ with Debye's, we see that

$$\Sigma \phi_1 f_1 = \frac{2\epsilon^2}{3DT} \sqrt{\frac{8\pi\epsilon^2 \rho_0}{DkTm_0}} c^{3/2} - \frac{1}{2} \cdot \frac{\epsilon^2 a}{DT} \cdot \frac{8\pi\epsilon^2 \rho_0}{DkTm_0} \cdot c, \quad (8)$$

where ρ_0 and m_0 are the mean density and the mean mass of one molecule of the solution.

Hence $\quad f_1 = c^{3/2}, \; f_2 = c^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$

and $\quad \phi_1 = AD^{-3/2}T^{-3/2}\rho_0^{1/2}, \; \phi_2 = BD^{-2}T^{-2}\rho_0 a. \quad . \quad (10)$

Again, Debye and Hückel give for the total energy of a solution per unit volume:

$$U = U_k + U_e = U_k - \frac{n\epsilon^2}{D} \cdot \frac{\kappa}{1 + a\kappa},$$

and comparing this with Cavanagh's expression (5) we see that

$$\left. \begin{array}{l} u_1 = -\frac{3}{2}AD^{-3/2}T^{-1/2}\rho_0^{1/2} \\ u_2 = -2BD^{-2}T^{-1}\rho_0 a \end{array} \right\}, \quad . \quad . \quad . \quad (11)$$

and hence the conditions $\dfrac{\partial \phi}{\partial T} = \dfrac{u}{T^2}$ will only be satisfied if

$$\frac{D^3}{\rho_0} = \text{const. and } \frac{D^2}{a\rho_0} = \text{const. or } aD = \text{const.} \quad (12)$$

Now these conditions might conceivably be satisfied over a small range of temperature, but in the equation from which they are derived, viz.:

$$\phi = K - \frac{u}{T} + \int \frac{du}{T^2},$$

the integral extends over the whole range of temperature necessary to bring the solution into the perfect gaseous state. Under such conditions it is obviously impossible that these equations should be obeyed.

Milner, on the other hand, assumes Clausius' virial equation for a gas to apply to osmotic pressure, which is a procedure by no means obviously justifiable, and one which, as Cavanagh himself points out, breaks down completely for a virial of the form $Nuc^{1/3}$ (as in the erroneous theory of Ghosh).

The procedure can also be easily shown to be inapplicable to a virial of the form Nuc^{a}, which represents Milner's calculations approximately if α is between $0\cdot47$ and $0\cdot5$. The intractability of Milner's function $f(h)$ prevents an accurate determination of the necessary thermodynamical conditions, but it is quite evident that they will not be fulfilled any more nearly than those required by the theory of Debye and Hückel.

Consider now the depression of the freezing-point of a solution, which according to Debye is given by

$$j = \frac{\epsilon^2}{6\mathrm{D}k\mathrm{T}} \cdot \sqrt{\frac{8\pi\epsilon^2}{\mathrm{D}k\mathrm{T}}} \cdot n^{1/2} = \mathrm{A}\mathrm{C}^{1/2} \,*. \quad . \quad . \quad (13)$$

for low concentrations, where $j = 1 - \theta/2\lambda\mathrm{C}$,

and $\mathrm{C} =$ concentration in gram molecules per litre, $= \dfrac{1000n}{\mathrm{N}}$,

$\lambda = 1\cdot858$, the molal lowering at infinite dilution.

$\theta =$ observed depression ;

and at higher concentrations by

$$j = \mathrm{A}\mathrm{C}^{1/2} - \mathrm{B}\mathrm{C}, \quad . \quad . \quad . \quad . \quad (14)$$

where B is adjustable, since it depends on the ionic radius.

But this value of j is obtained by differentiating Φ, so that it is evident from the above reasoning that the numerical values of the coefficients A and B are illusory, and all that we are entitled to assume as the result of Debye's calculation of U_e is that j is of the form :

$$j = \phi_1 c^{1/2} + \phi_2 c = \phi_1' \mathrm{C}^{1/2} + \phi_2' \mathrm{C}, \quad . \quad . \quad (15)$$

where ϕ_1, ϕ_2 are indeterminate functions of T and p.

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* Taking the values $\mathrm{D} = 88\cdot23$ at $0°$ C., $\mathrm{N} = 6\cdot06 \times 10^{23}$, $\epsilon = 4\cdot774 \times 10^{-10}$ E.S.U., $k = 1\cdot371 \times 10^{-16}$ erg/deg., $\mathrm{T} = 273\cdot1$, A becomes $0\cdot373$.

In the same way Milner gives

$$j = \tfrac{1}{6} h f(h) = \beta c^a \text{ approx.,} \quad . \quad . \quad . \quad . \quad (16)$$

but all we can really deduce from Milner's value of U_e is that

$$j = \phi c^a \text{ approx.,} \ = \phi' C^a, \quad . \quad . \quad . \quad . \quad (17)$$

where ϕ is similarly indeterminate.

Thus the only way in which experiment can help us to decide between equations (1) and (2) is by settling whether the observed facts are represented better by curves of the shape (15) or (17); and in this connexion it is instructive to note that whereas Lewis and Linhart * obtained the empirical rule

$$j = \beta C^a, \text{ in agreement with (17),}$$

Brönsted †, working independently with the same series of uni-univalent salts, concluded that the facts were fitted best by a formula of the type

$$j = 0.32\, C^{1/2} - \beta C, \text{ in agreement with (15).}$$

This illustrates very plainly the difficulty of deciding between the two types of curve in the present state of experimental knowledge.

Quite recently, however, some accurate measurements of j in very dilute aqueous solutions of hydrogen and thallous chlorides have been carried out by Randall and Vanselow ‡. Scatchard § attempted to show that these results were in agreement with Debye's theory by assuming (1) that the ionic radius term became important at much lower concentrations than were contemplated by Debye himself (D. & H., *loc. cit.* p. 202), and (2) that the j–$C^{1/2}$ curve touched the limiting Debye formula (13) for infinite dilutions ‖. In this way he obtained the equation :

$$j = 0.38\, C^{1/2} - 0.85\, C \text{ for HCl.}$$

We have found similarly for thallous chloride, using Scatchard's assumptions,

$$j = 0.372\, C^{1/2} - 0.8\, C,$$

and the values of j found from these equations are given in columns (5) and (8) of the table.

The results calculated from Milner's formula, on the other

* J. A. C. S. xli. p. 1952 (1919).
† *Ibid.* xliv. p. 938 (1922).
‡ J. A. C. S. xlvi. p. 2418 (1924). § *Ibid.* xlvii. p. 641 (1925).
‖ This is a pure assumption, since the limiting Milner formula has a different slope.

hand, which for comparison with (13) and for ease in computation may be written

$$j = \frac{A h f'(h)}{\sqrt{3h^3}} \ \sqrt{e} = A(F)C \sqrt{\bar{C}},$$

where $h = 1.186\ C^*$, are given in column (3).

Randall and Vanselow's readings were then plotted on a large scale against $C^{1/2}$, and a smooth curve was drawn through them, from which the values of j given in column (3) were read off at round concentrations.

TABLE.

C.	$\dfrac{h f(h)}{\sqrt{3h^3}}$	j Milner.	j Debye eq. (13).	j Debye eq. (18).	j obs. HCl.	j Debye eq. (19).	j obs. TlCl.
·0005	0·727	·006	·008	·008	·007	·008	·007
·0007	0·725	·007	·010	·009	·008	·009	·008
·001	0·723	·009	·012	·011	·009	·011	·010
·002	0·716	·012	·017	·015	·013	·015	·014
·005	0·704	·019	·026	·023	·021	·022	·022
·007	0·701	·022	·031	·026	·025	·026	·026
·01	0·696	·026	·037	·030	·030	·031	·031

It will be seen that, for the lowest concentrations, where if at all the theories would be expected to hold good, Milner's theory gives at least as good a representation of the facts as Debye's, but without the aid of an adjustable constant; the actual curve lies about halfway between the two theoretical ones.

It was found to be fitted best by the equations:

$$j = 0.30\ C^{1/2} \quad \text{for HCl}$$
$$\text{and} \qquad j = 0.305\ C^{1/2} \text{ for TlCl},$$

which, as we should expect from the foregoing analysis, do not agree numerically with either of the two theories. Nor can these equations be definitely assigned to one or other of the types (15) or (17), which represent the form of j according to these theories. Hence it seems that at present experimental evidence is insufficient to decide between them.

Balliol College,
   Oxford.

* Milner gives $h = 1.203\ C$, but using more accurate modern values for ϵ, D, k, and T, we get the above result for water at 0° C.

LXXIX. *The Activity Coefficients and Transport Number of Solutions of Hydrogen Chloride in Methyl Alcohol. By* GORDON NONHEBEL, *B.A.,* and HAROLD HARTLEY, *M.A., Balliol College, Oxford* *.

ALTHOUGH the electrical conductivities of numerous solutions of electrolytes in non-aqueous solvents have been studied in some detail, electromotive force measurements leading to a knowledge of activity coefficients have been much neglected, the only recent work being that of Pearce and Hart † on solutions of lithium chloride in various alcohols, and the measurements of Danner ‡ and of Harned § on solutions of hydrogen chloride in ethyl alcohol. A study of activity coefficients in solvents of widely differing dielectric constants is of particular interest in view of the theoretical expressions derived by Milner ‖ and by Debye and Hückel ¶ for their variation with concentration and solvent. Pike and Nonhebel ** have recently shown that we cannot, on thermodynamical grounds, expect either of these two theories to predict more than the general shape of the activity coefficient curve. We shall show in a later part of this paper that the E.M.F. data for hydrogen chloride in three different solvents yield activity coefficients which are not in agreement with Debye, but which are in sufficiently good agreement with Milner to make his expression serve at least as a useful empirical equation.

G. N. Lewis †† defines the mean activity a of the ions and the activity a_2 of the undissociated portion of the univalent electrolyte by the equation :

$$\overline{F} - \overline{F}_0 = 2RT \ln a = RT \ln a_2, \quad . \quad . \quad (1)$$

where $\overline{F}$ is the partial molal free energy of the electrolyte in any given state, and $\overline{F}_0$ its partial free energy in a standard state, chosen for each solvent and for each temperature so that the mean activity of the ions is equal to unity. Then

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* Communicated by Dr. J. W. Nicholson, F.R.S.

† Journ. Amer. Chem. Soc. xliv. p. 2411 (1922).

‡ Journ. Amer. Chem. Soc. xliv. p. 2832 (1922).

§ Journ. Amer. Chem. Soc. xlvii. p. 87 (1925).

‖ Phil. Mag. xxiii. p. 351 (1912); xxv. p. 742 (1913).

¶ *Phys. Zeits.* xxiv. p. 185 (1923); xxv. p. 97 (1924).

** *Suprà*, p. 723.

†† Journ. Amer. Chem. Soc. xliii. p. 1112 (1921) ; Lewis and Randall, 'Thermodynamics and Free Energy,' pp. 255 & 326.

if f is the activity coefficient when concentrations are expressed in mols per litre of solution, we may write

$$a = fc. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The activity coefficients of hydrogen chloride in methyl alcohol solution at 25° C. have been determined by a series of measurements of the E.M.F. of cells of the type
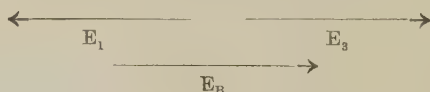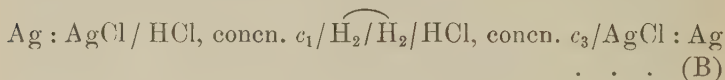
$$H_2/HCl \text{ in } MeOH/AgCl : Ag \quad . \quad . \quad . \quad (A)$$
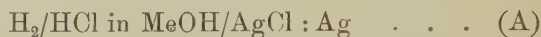
over a wide range of concentration. For such cells we have

$$\overline{F} - \overline{F}_0 = (E_0 - E)\mathbf{F} = 2RT \ln cf, \quad . \quad . \quad . \quad (3)$$

where $\mathbf{F}$ is the value of the faraday. By a method of graphical extrapolation to infinitely small concentrations, where f is assumed to be unity, the value of E_0 can readily be obtained.

The transport number η_H of the cation is obtained by measuring a cell of the type

$$Ag : AgCl / HCl, \text{ concn. } c_1 / \overbrace{H_2 / H_2} / HCl, \text{ concn. } c_3 / AgCl : Ag$$
$$. \quad . \quad . \quad (B)$$

$$\xleftarrow{\hspace{3cm}} \quad \xrightarrow{\hspace{3cm}}$$
$$E_1 \qquad\qquad E_3$$
$$\xrightarrow{\hspace{4cm}}$$
$$E_B$$

for which we have

$$E_B = E_3 - E_1 = \frac{2RT}{\mathbf{F}} \ln \frac{a_1}{a_3} \quad . \quad . \quad . \quad . \quad (4)$$

and a cell with a liquid junction

$$Ag : AgCl / HCl, \text{ concn. } c_1 / HCl, \text{ concn. } c_3 / AgCl : Ag, \quad (C)$$

for which the equation is

$$E_C = \frac{2\eta_H RT}{\mathbf{F}} \ln \frac{a_1}{a_3}, \quad . \quad . \quad . \quad . \quad (5)$$

whence $\eta_H = E_C / E_B$.

Experimental.

Owing to the large influence of traces of water on the activity of the hydrogen ion, the magnitude of which is shown later, it was essential that the solvent used should be absolutely dry, and that every possible precaution should be taken to prevent entrance of moisture into the solution during the progress of a measurement. The alcohol was

obtained by the method described by Hartley and Raikes *. The more concentrated solutions of hydrogen chloride were prepared by absorption in the alcohol of the dry gas (obtained by action of pure sulphuric acid on dry sodium chloride and subsequent passage through suitable spray traps). Their concentrations were determined by weight titration against baryta, methyl red being used as indicator : the baryta was standardized against constant boiling aqueous hydrochloric acid †. The more dilute solutions were obtained by weight dilution.

Since at 25° C. the rate of esterification of 0·1 N hydrochloric acid in methyl alcohol solutions is 0·63 per cent. per day, with a temperature coefficient of 16 per cent. per degree ‡, all measurements with solutions of greater concentration than 0·01 N were made within twenty-four hours of their preparation.

The silver-silver chloride electrodes were prepared exactly as described by MacInnes and Beattie § except that they were chloridized in a 0·1 N alcoholic solution of sodium chloride, alcoholic hydrogen chloride being unsuitable for the purpose as the electrodes were not then reproducible. Two electrodes were used in each solution ; they were freshly prepared for each measurement. Their potential against calomel electrodes ‖, using alcoholic sodium chloride as electrolyte in two half cells of type C, fig. 1, was 0·0467 ± ·0002 volt. This is in good agreement with the values 0·0466 and 0·0468 obtained by Linhart and by Horsch ¶ respectively : the low value of 0·0455 obtained by Gerke ** was probably due to poisoning of the silver chloride electrodes by the calomel. Poisoning was certainly observed in methyl alcoholic solutions when an H cell, similar to Gerke's, was used.

The hydrogen electrodes were of the iridized gold plate type described by Lewis, Brighton, and Sebastian †† ; they soon lost their catalytic activity in alcoholic solutions, and were therefore freshly iridized before each measurement. The hydrogen was obtained by electrolysis of alkali (free

* Journ. Chem. Soc. cxxvii. p. 524 (1925).

† Foulk & Hollingsworth, Journ. Amer. Chem. Soc. xlv. p. 1220 (1923).

‡ Woolcock & Murray-Rust, unpublished.

§ Journ. Amer. Chem. Soc. xlii. p. 1117 (1920).

‖ The calomel was prepared electrolytically from twice distilled mercury (Ellis, Journ. Amer. Chem. Soc. xxxviii. p. 737, 1916).

¶ Journ. Amer. Chem. Soc. xli. p. 1175 (1919) ; *ibid.* p. 1790.

** Journ. Amer. Chem. Soc. xliv. p. 1684 (1922).

†† Journ. Amer. Chem. Soc. xxxix. p. 2245 (1917).

from carbonate); it was freed from traces of oxygen by passage over a red-hot tungsten filament and dried by sulphuric acid, soda lime, and phosphorus pentoxide.

Fig. 1 A shows the vessel used for measurements of the E.M.F. of cells of the type H_2/HCl in MeOH/AgCl : Ag ; in order to eliminate errors in dilute solution it was made of orosilicate glass (durosil). a is the hydrogen electrode, which is carried by an " outside ground " glass cap. Before insertion in the cell, it was soaked in some of the solution in the vessel D, which had an identical grind. The hydrogen was saturated with alcohol vapour by a bubbler of the Lewis type [*], which was attached to the electrode vessel by means

Fig. 1.
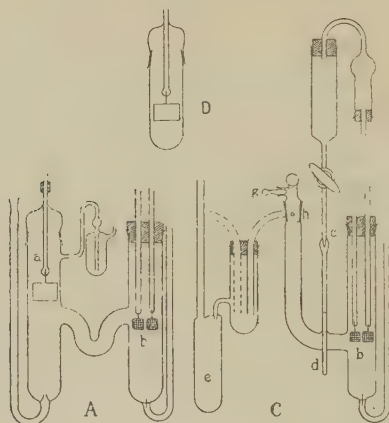
of a ground joint held tight by an external piece of rubber tubing. The silver-silver chloride electrodes are shown at b; they were held in rubber bungs which had been freed from sulphur. About five hours were required for the hydrogen electrodes to come to equilibrium ; and a measurement was not accepted unless a cell showed a constant E.M.F. for over two hours.

For the measurement of cells with a liquid junction, the vessels shown in fig. 1 C were used. In order to obtain reproducible results a simple type of flowing liquid junction [†] was used ; the dripper c allowed a slow but constant flow of liquid through the cell, and this liquid was warmed to the temperature of the bath by the single coil

[*] Journ. Amer. Chem. Soc. xxxix. p. 2245 (1917).
[†] See Lamb & Larson, Journ. Amer. Chem. Soc. xlii p. 229 (1920).

d : the excess liquid flowed away into the reservoir e. In this manner perfectly reproducible results could be obtained, the E.M.F. of a cell remaining constant to 0·1 mv. for over six hours ; though if the flow were stopped, the boundary showed perceptible ageing. The design of the tap h minimized the effect of the high electrical resistance of the solution ; its stopper g permitted the removal of the bubble of air. A carefully purified mixture of 5 per cent. of paraffin wax with vaseline was used as tap grease : this was practically insoluble in the alcohol.

The paraffin thermostats, electrical shielding, and potentiometer were similar to those described by Lewis and Brighton. The resistances of the potentiometer and the E.M.F. of the Weston cells were checked against standards bearing N.P.L. certificates. All the measurements were carried out at $25 \pm ·02°$ C.

RESULTS.

E.M.F. of Cells $H_2/HCl/AgCl : Ag$.

In Table I. below, the E.M.F.'s of the hydrogen cells have been corrected to a partial pressure of one atmosphere of hydrogen, the vapour pressure of methyl alcohol being taken as 126·4 mm. at $25°$ C.* Concentrations M are expressed in mols per 1000 grams of solvent.

TABLE I.

E.M.F. of Cells H_2/HCl in Methyl Alcohol/$AgCl : Ag$.

M.	E (volt).	M.	E (volt).	M.	E (volt).
0·0004955	0·3861	0·009857	0·2445	0·07332	0·1618
·001652	·3274	·01444	·2285	·07333	·1618
·002363	·3098	·01722	·2207	·07507	·1612
·002683	·3041	·01986	·2150	·09467	·1521
·002980	·2999	·02363	·2079	·1155	·1439
·003161	·2957	·02549	·2049	·4802	·0892
·004939	·2757	·04261	·1833	·5574	·0844
·005425	·2712	·04356	·1828		
·007113	·2598	·05312	·1758		

The activity coefficients calculated from these results are given in Table IV.

* H. G. Smith, unpublished.

Influence of Water.

To test this, a drop of water was added to each limb of some of the cells after they had come to equilbrium, making its concentration in the solutions approximately 0·055 per cent. (0·028 volume normal). The effect on the E.M.F. is shown in Table II.

Table II.

Influence of moisture on the Cells H_2/HCl in MeOH/AgCl : Ag.

M.	E dry (volts).	E wet (volts).	Increase in E (millivolts).	γ dry.	γ wet.
0·01571	0·2253	0·2300	4·7	0·532	0·486
·04261	·1833	·1867	3·4	·444	·416
·05312	·1758	·1790	3·2	·413	·388
·4802	·0892	·0903	1·1	·246	·241
·5574	·0844	·0854	1·0	·233	·228

It will be observed that the increase in E.M.F. is quite reproducible, and, as we should expect, the effect is greater in the more dilute solutions of the hydrogen chloride since the relative concentration of the water is larger. Since in very dilute solutions 0·01 per cent. water raises the E.M.F. by over one millivolt, the difficulty of obtaining results accurate to more than 0·3 mv. will be realized.

The change in the molal activity coefficients γ (see p. 741) is shown in columns 5 and 6.

Transport Numbers.

The transport number data are shown in Table III.; in the first column are given the geometrical mean molalities to which η_H of equation (5) corresponds, the second and third give the molalities corresponding with the activities a_1 and a_3, and the fourth gives the E.M.F. E_C of the cell with the liquid junction. The E.M.F. E_B of the concentration cell without a liquid junction was obtained from a large scale plot of $(E_A + 0.11831 \log M)$, using all the results given in Table I. As shown in the table, the presence of water diminishes η_H, since it almost certainly combines with the hydrogen ions in the solution; its uneven distribution in the cells may, however, raise the observed value of the transport number. The values of η_H shown in the table are

somewhat irregular for this reason, and are accurate only to 0·005: in very dilute solutions the most probable value is 0·735 ± ·005.

TABLE III.
Transport Number of the Hydrogen Ion.

$\sqrt{M_1 M_3}$.	M_1.	M_3.	E_C.	E_B.	η_H.
0·00447	0·01571	0·001274	0·0844	0·1153	0·732
·00746	·02549	·002186	·0802	·1090	·736
·00864	·02363	·003161	·0652	·08845	·737
·0154	·04356	·005425	·0657	·0885	·742
·0190	·07332	·004939	·0852	·1139	·748
·0206	·07507	·005671	·0804	·1081	·744
·0248	·07333	·008396	·0672	·0900	·747
·0260	·09467	·007113	·0801	·1077	·744
·0337	·1155	·009857	·0751	·1005	·747
·0385	·1070	·01381	·0614	·0828	·742
·143	·4802	·04261	·0709	·0946	·749
(·143	+0·055 %	water	·0719	·0964	·746)
·155	·5574	·04303	·0689	·0914	·761
(·155	+0·055 %	water	·0699	·0936	·747)

In dilute aqueous solutions at 25° C., η_H has the value 0·830, which also rises slightly as the concentration is increased [*]. In solutions in ethyl alcohol, however, Harned [†] found that the transport number varied very considerably and in the opposite direction with change in concentration: in dilute solution its value is 0·75 approximately.

COMPARISON OF THE THEORIES OF MILNER AND DEBYE WITH EXPERIMENT.

Calculation of the Activity Coefficients of Hydrogen Chloride in Water, Methyl and Ethyl Alcohols.

The expression obtained by Debye for the activity coefficient of the ions of a uni-univalent electrolyte in a solution of dielectric constant D and at a temperature T, is :—

$$-\log_{10} f = \frac{0·4343\, \epsilon^3\, \sqrt{2\pi N}}{(DkT)^{3/2}\, \sqrt{1000}}\, \sqrt{c} = A\, \sqrt{c}, \quad . \quad . \quad (6)$$

[*] France & Moran, Journ. Amer. Chem. Soc. xlvi. p. 21 (1924), and Noyes & Falk, *ibid.* xxxiii. p. 1436 (1911).
[†] Journ. Amer. Chem. Soc. xlvii. p. 87 (1925).

where ϵ is the charge on an electron, N is Avogadro's number, k is the Boltzmann gas constant per molecule, and c is the concentration of the solute expressed in mols per litre of solution. If the size of the ions is not neglected, then

$$-\log f = A \sqrt{c} - Bc, \quad . \quad . \quad . \quad (6\,a)$$

where A is the same constant, depending only on the solvent, and B is adjustable. Since in 0·01 N aqueous solution there are approximately 1400 molecules of solvent to every ion of solute, the effect of the size of the ions should not be very appreciable.

Writing

$$\epsilon = 4\cdot77 \times 10^{-10} \text{ E.S.U.}, \quad N = 6\cdot06 \times 10^{23},$$
$$k = 1\cdot371 \times 10^{-16} \text{ erg/deg.},$$

and taking the dielectric constants of water, methyl and ethyl alcohols at 25° C. as 78·77, 30·3, and 25·0 respectively, the value of the constant A for the three solvents becomes in turn 0·5037, 2·112, and 2·818.

Milner's theory gives for the virial or mutual potential energy of a mixture of uni-univalent ions,

$$W = RT\, h f(h),$$

where

$$h = \frac{1}{10} \cdot \left(\frac{8\pi N c}{3}\right)^{1/3} \cdot \frac{\epsilon^2}{DkT}, \quad . \quad . \quad . \quad (7)$$

where $f(h)$ is a tabulated function whose values are not determinable with any great accuracy. From this the expression for the activity coefficient may be obtained on the assumption that $h f(h)$ varies directly as c^α, which is only approximately true. For the decrease in free energy when one mol both of positive and negative ions is transferred from a solution of osmotic pressure P, in which the concentration of each ion is c, to one of osmotic pressure P_0, where the concentration c_0 is so small that the interionic attraction is negligible, is

$$-\Delta F = \int_{P_0}^{P} V\,dP.$$

But by applying the virial equation of Clausius, and remembering that there are two gm. ions in a volume V, we have

$$PV = 2RT - \tfrac{1}{3}RT\,h f(h)$$

or

$$P = 2RT c - \tfrac{1}{3}\beta c^{\alpha+1}$$

where $\beta c^\alpha = RT\,h f(h),$

whence

$$-\Delta F = 2RT \ln \frac{c}{c_0} - \frac{\alpha+1}{3\alpha}\,\beta c^\alpha.$$

But from eqn. (3),

$$-\Delta F = 2RT \ln \frac{cf}{c_0 f_0}$$

and f_0 is equal to unity, so that

$$-\ln f = \frac{\alpha+1}{3\alpha} \cdot \tfrac{1}{2} h f(h). \quad . \quad . \quad . \quad (8)$$

The average slope of the $\log h f(h) / \log c$ curve gives a value of $\alpha = 0.487$, hence, as an approximation, we have:

$$-\ln f = 1.018 \cdot \tfrac{1}{2} h f(h).$$

For comparison with (6), and for ease in computation, we may re-write this in the form [*]

$$-\log f = 1.018 \, A \cdot \frac{h f(h)}{\sqrt{3 h^3}} \, \sqrt{c}$$

$$= 1.018 \, A \, f(c) \cdot \sqrt{c}. \quad . \quad . \quad . \quad (9)$$

Owing to slight irregularities in the values of $hf(h)$ given by Milner, it was necessary to smooth the curves of $f(c) / \sqrt{c}$, and in consequence the values of $f(c)$ quoted in Tables V., VIII., and X. may be in error by ± 0.002. In relatively concentrated aqueous solutions and in solutions in the alcohols this may affect the calculated activity coefficient by at most ± 0.002, but this is immaterial as the experimental error in the alcoholic solutions is somewhat greater.

Inserting numerical values in the relation between h and c (eqn. 7) we find that at 25° C., $h = 1.217 \, c^{1/3}$ for aqueous solutions, and $h = 3.164 \, c^{1/3}$ and $h = 3.835 \, c^{1/3}$ for solutions in methyl and ethyl alcohols respectively.

The fairest method of testing these theories by experiment is to calculate the value of E_0 in the equation

$$E = E_0 - 0.11831 \log cf \quad \text{(from eqn. 3)}, \quad . \quad (10)$$

and see whether it is constant within the experimental error.

Solutions in Methyl Alcohol.

The results of such calculations for the experimental data of Table I. are given in Table IV. Since the densities of the solutions are unknown, the volume concentrations c were obtained by multiplying the concentrations per 1000 g. of solution by 0.7864, the density of the pure alcohol [†]. In the

[*] *Cf.* A. A. Noyes, Journ. Amer. Chem. Soc. xlvi. p. 1080 (1924).
[†] Hartley & Raikes, Journ. Chem. Soc. cxxvii. p. 524 (1925).

TABLE IV.

Calculation of E_0 for the Cell H_2/HCl in $MeOH/AgCl : Ag$.

C.	Milner.		Debye.	$-E_{0A}.$	$-E_0'.$	f obs. if $E = -0.0205.$
	f, eqn. 9.	$-E_0$, eqns. 9. & 10.	$-E_0$, eqns. 6 & 10.			
0.0003897	0.934	0.0208	0.0222	0.0193	0.0172	0.938
.001299	.885	.0204	.0229	.0178	.0141	.883
.001858	.865	.0207	.0240	.0178	.0133	.869
.00211	.857	.0204	.0240	.0173	.0125	.856
.002343	.850	.0196	.0233	.0164	.0113	.836
.002486	.846	.0210	.0249	.0178	.0124	.854
.003883	.813	.0202	.0250	.0163	.0095	.807
.004265	.805	.0204	.0255	.0163	.0091	.801
.005592	.781	.0194	.0264	.0149	.0067	.765
.007749	.749	.0201	.0271	.0148	.0053	.744
.01135	.707	.0194	.0282	.0131	.0016	.692
.01353	.686	.0197	.0294	.0127	.0004	.676
.01561	.669	.0193	.0300	.0119	− .0013	.654
.01857	.647	.0194	.0310	.0110	− .0032	.631
.02003	.637	.0192	.0314	.0105	− .0040	.621
.03346	.566	.0205	.0370	.0091	− .0086	.568
.03420	.563	.0202	.0369	.0086	− .0093	.560
.04169	.533	.0198	.0384	.0067	− .0126	.525
.05750	.484	.0223	.0448	...	− .0150	.501
.05888	.480	.0220	.0449	...	− .0157	.494
.07419	.443	.0233	.0496	...	− .0184	.469

second column of the table are given values of f calculated from equation (9) : these are used for the calculation of E_0 (Milner) shown in column 3. Values of E_0 (Debye) were calculated from equations (6) and (10). E_{0A} is the value of E_0 calculated on the assumption that f is equal to Λ_c/Λ_0, the conductivity " degree of dissociation," the latter being obtained from a plot of Λ_c against $\sqrt{c}$ *. E_0' is the value of E_0 calculated on the assumption of complete dissociation and no interionic forces ($f=1$).

It will be seen that the values of E_0 (Milner) are nearly

* Data from W. F. K. Wynne-Jones, unpublished, and H. Goldschmidt, *Zeit. Phys. Chem.* cviii. p. 121 (1924).

constant within the experimental error, passing through a slight maximum at about 0·01 N, whereas the values calculated on the other assumptions vary continuously with the concentration, but converge to the true value of E_0 at infinite dilution. This is illustrated by fig. 2. The value of E_0 obtained by extrapolation of the four curves to the same point is $E_0 = -0·0205 \pm ·0003$ volt. Values of the activity coefficient calculated from equation (10) after insertion of this value are shown in the last column of the table.

Fig. 2.
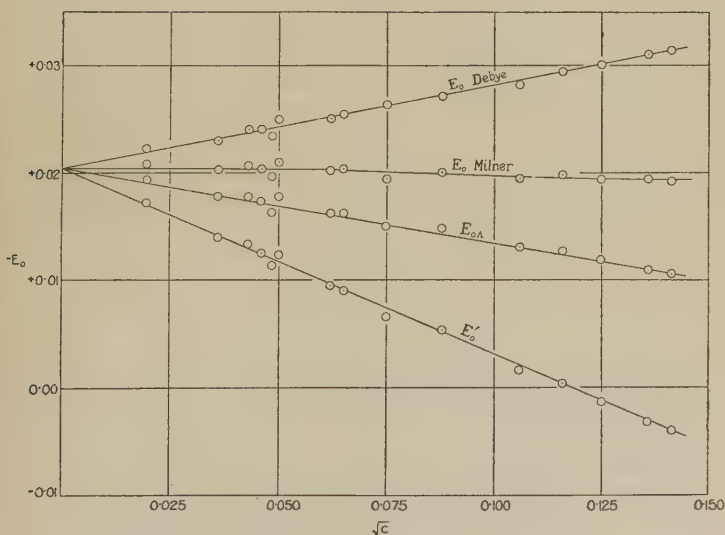
E_0 for cells H_2/HCl in Methyl Alcohol/AgCl : Ag.

In Table V., which is illustrated by fig. 3, are given smoothed values of f at round concentrations, obtained from large scale plots of $\log f$ and f against $\sqrt{c}$, together with values calculated from the theories of Milner and Debye. The fifth column gives the value of f calculated from Debye's limiting equation (6), and the sixth, values calculated on the assumption that the B coefficient in equation $(6 a)$ has the value 6 (chosen to fit the observed value at 0·01 N) : in both cases the agreement is bad. It is evident that it is the coefficient of $\sqrt{c}$ in Debye's limiting equation which is at

TABLE V.

Activities of Hydrogen Chloride in Methyl Alcohol solutions
at round concentrations.

C.	f, smoothed.	Milner.		Debye.		f from eqn. 11.	f from eqn. 12.	$\dfrac{\Lambda_c}{\Lambda_0}$
		$f(c)$.	f, eqn. 9.	f, eqn. 6.	f, eqn. 6a.			
0·0001	0·966	0·716	0·965	0·953	0·954	0·966	0·966	0·980
·0002	·953	·708	·952	·934	·936	·953	·953	·972
·0005	·927	·696	·926	·897	·903	·926	·927	·957
·001	·900	·686	·898	·858	·869	·898	·898	·938
·002	·861	·679	·860	·804	·827	·858	·859	·912
·005	·785	·669	·791	·709	·760	·785	·788	·860
·01	·707	·659	·722	·615	(·707)	·710	·714	·809
·02	·624	·644	·637	·503	·663	·616	(·624)	·754
·05	·516	·624	·501	·337	·673	·466	·480	·671
·10	·442	(·6)	·391	·215	·855	·339	·341	...

Fig. 3.

Comparison of Observed with Calculated Activity Coefficients.

fault; in fact the values of f are best represented by the empirical equation

$$-\log f = 1 \cdot 485 \sqrt{c}, \quad . \quad . \quad . \quad . \quad (11)$$

as shown in column 7. An equation of the form

$$-\log f = A' \sqrt{c} - B'c, \quad . \quad . \quad . \quad . \quad (12)$$

in which A' and B' have the values $1 \cdot 485$ and $0 \cdot 26$ respectively, will not represent the activity coefficient curve up to much higher concentrations, as the $\log f / \sqrt{c}$ curve turns off very sharply at about $0 \cdot 02$ N (column 8).

When the concentration is greater than $0 \cdot 05$ normal, we can no longer assume that the density of the solution is equal to the density of the pure solvent. It is therefore convenient to use a molal activity coefficient γ defined by the equation

$$M\gamma = a = cf,$$

where M is the concentration expressed in mols per 1000 g. of solvent. Table VI. contains values of this coefficient for concentrations of $0 \cdot 01$ M upwards in both methyl and ethyl alcohols.

TABLE VI.

Molal Activity Coefficients of HCl in Methyl and Ethyl Alcohols.

M.	γ, methyl.	γ, ethyl.	M.	γ, ethyl.
0·01	0·583	0·537	0·70	0·168
·02	·514	·456	1·0	·148
·05	·426	·364	1·5	·135
·10	·363	·300	2·0	·131
·20	·314	·244	3·0	·129
·50	·243	·187		

Note that the activity coefficient curve in ethyl alcohol passes through a minimum between two and three molal.

Solutions in Water.

The E.M.F. of cells H_2/HCl, aq./$AgCl : Ag$ at $25°$ have been measured up to a concentration of $1 \cdot 5$ molal [*], and of

* Noyes & Ellis, Journ. Amer. Chem. Soc. xxxix. p. 2532 (1917); Linhart, *ibid.* xli. p. 1175 (1919); Scatchard, *ibid.* xlvii. p. 641 (1925).

cells H_2/HCl, aq./Hg_2Cl_2/Hg up to 16 molal [*] : the latter may be compared with the former by the subtraction of 0·0466 volt. For the calculation of the molal activity co-efficients γ from the equations of Milner and Debye, we may assume without error that the density of the dilute solutions is unity. Table VII. gives the various values of E_0 calculated on this assumption and is exactly analogous to Table IV.

TABLE VII.

Calculation of E_0 for the Cell H_2/HCl aq./AgCl : Ag.

M.	E observed (volt).	Milner		Debye E_0, eqns. 6 & 10.	E_{0A}.	E_0'.	γ, if $E_0 =$ 0·2229.
		γ.	E_0.				
Linhart.							
0·000136	0·6805	0·990	0·2225	0·2224	0·2233	0·2231	0·996
·000242	·6514	·987	·2229	·2227	·2234	·2236	·987
·000483	·6161	·981	·2228	·2225	·2237	·2238	·983
·001	·5791	·973	·2228	·2223	·2251	·2242	·975
·004826	·5002	·944	·2232	·2221	·2259	·2262	·938
·00965	·4658	·922	·2232	·2215	...	·2274	·916
·04826	·3874	·839	·2227	·2185	...	·2317	·843
Noyes & Ellis.							
·000999	·5789	·973	·2225	·2220	...	·2240	·979
·003378	·51696	·953	·2221	·2212	...	·2246	·967
·00948	·46666	·923	·2232	·2216	...	·2273	·918
·03324	·40545	·864	·2230	·2197	...	·2306	·862
·09534	·35453	·783	·2213	·2154	...	·2338	·809
·33314	·29348	·640	·2141	·2026	...	·2370	·760
Scatchard.							
·01002	·46376	·921	·2230	·2213	·2257	·2273	·918
·01010	·46331	·921	·2230	·2212	·2256	·2272	·920
·01031	·46228	·920	·2230	·2212	·2257	·2272	·919
·4986	·38582	·837	·2226	·2184	·2285	·2318	·842
·5005	·38568	·837	·2226	·2185	·2286	·2318	·831
·9642	·35393	·782	·2211	·2153	...	·2338	·810
·9834	·3532	·780	·2213	·2153	...	·2340	·806

The conductivity ratio was calculated from the data of Bray and Hunt [†]. As in the case of methyl alcohol solutions,

[*] Ellis, Journ. Amer. Chem. Soc. xxxviii. p. 737 (1916); Linhart, *ibid.* xxxix. p. 2601 (1917).
[†] Journ. Amer. Chem. Soc. xxxiii. p. 781 (1911).

E_0 (Milner) passes through a slight maximum at about 0·01 N. Extrapolation of the four curves gives

$$E_0 = 0·2229 \pm ·0001 \text{ volt.}$$

This is in good agreement with the value 0·02230 deduced by Randall and Vanselow * from a combination of their freezing-point measurements with the E.M.F. determinations of Linhart. Scatchard † extrapolated E_0' to the value 0·2226 volt by assuming that Debye's limiting equation was obeyed exactly by the most dilute solutions only : it is evident from the table that this is not so, since E_0 (Debye) is not constant.

Table VIII., similar to Table V., gives values at round

TABLE VIII.

Activity coefficients of Aqueous HCl at round concentrations.

	γ, smoothed.	Milner.		Debye.		γ calc., eqn. 14.	$\dfrac{\Delta_c}{\Delta_0}$.	γ, from F. pts.
		$f(c)$.	γ, eqn. 9.	γ, eqn. 6.	γ, eqn. 6a.			
0·0001	0·991	0·734	0·991	0·989	0·989	0·992	0·997	0·992
·0002	·988	·732	·988	·984	·985	·988	·995	...
·0005	·981	·727	·981	·974	·977	·981	·993	·981
·001	·973	·722	·973	·964	·969	·974	·990	·973
·002	·962	·716	·963	·950	·958	·963	·986	·962
·005	·942	·704	·943	·921	(·942)	·942	·979	·940
·01	·919	·696	·921	·891	·932	·919	·970	·916
·02	·889	·685	·892	·849	·931	·888	·958	·884
·05	·841	·675	·837	·772		·829	·939	·840
·10	·807	·670	·779	·693		·767	·920	·809
·2	·779							·782
·30	·767							
·40	·764							
·50	·768							
·80	·794							
1·0	·822							
2·0	1·02							
3·0	1·35							
4·0	1·77							

* Journ. Amer. Chem. Soc. xlvi. p. 2118 (1924).
† Journ. Amer. Chem. Soc. xlvii. p. 641 (1925).

concentrations of γ observed and calculated. The sixth column contains values of γ calculated from equation ($6\,a$) if $B = 2\cdot0$, and the seventh, values calculated from the empirical equation

$$-\log\gamma = 0\cdot365\sqrt{\overline{M}}. \quad . \quad . \quad . \quad (14)$$

In the eighth column are given values of the activity co-efficients calculated by Randall and Vanselow from their freezing-point measurements with the aid of the empirical relationship $j = \beta M^{\alpha}$ for the osmotic deviation coefficient; the agreement of γ (Milner) with the activity coefficients of the alkali halides and nitrates (given by Lewis and Randall, 'Thermodynamics,' p. 344) is equally good.

Solutions in Ethyl Alcohol.

Table IX. shows the various values of E_0 for the cell H_2/HCl in ethyl alcohol/AgCl : Ag, calculated from the data of Danner [*] and of Harned [†]. The former worker

TABLE IX.

Calculation of E_0 for the Cell $H_2\,/\,HCl$ in Ethyl Alcohol / AgCl : Ag.

C.	E obs. (volt).	Milner.		Debye. $-E_0$, eqns. 6 & 10.	$-E_{0\Delta}$.	$-E_0'$.	f, if $E_0 = 0\cdot0575$.
		f, eqn. 9.	$-E_0$, eqns. 9 & 10.				
0·0007851	0·3053	0·881	0·0685	0·0714	0·0680	0·0621	...
·001570	·2770	·838	·0638	·0679	·0634	·0547	0·947
·003925	·2392	·760	·0596	·0663	·0597	·0454	·790
·007851	·2109	·683	·0577	·0677	·0575	·0381	·686
·00886	·2056	·667	·0580	·0687	·0576	·0373	·675
·0139	·1882	·608	·0571	·0708	·0560	·0315	·603
·0157	·1830	·591	·0575	·0722	·0562	·0304	·590
·01955	·1746	·560	·0584	·0742	·0554	·0275	·558
·0274	·1607	·510	·0588	·0794	·0552	·0241	·522
·03321	·1548	·481	·0578	·0809	·0532	·0202	·484
·03925	·1484	·456	·0584	·0841	·0528	·0179	·463

[*] Journ. Amer. Chem. Soc. xliv. p. 2832 (1922).
[†] Journ. Amer. Chem. Soc. xlvii. p. 87 (1925).

used calomel electrodes, but his results can be converted to those of Harned with silver-silver chloride electrodes by the subtraction of 0·0350 volt. Actually, since the potential between calomel and silver chloride electrodes is independent of the solvent, the difference should be 0·0467 volt, a fact which points to some error in one or both series of measurements. The densities of the dilute solutions have been taken as 0·7851 *, those of the more concentrated solutions have been interpolated from the data of Jones and Lapworth† The values of Λ_c were taken from a plot of Goldschmidt's ‡ results against $c^{1/2}$. Neglecting the E.M.F.'s for the three most dilute solutions, which from the shape of the curves are obviously in error, we obtain by extrapolation

$$E_0 = -0·0575 \pm ·0005 \text{ volt.}$$

Values of the activity coefficients f at round concentrations are given in Table X., together with those calculated from the empirical equation

$$-\log f = 1·88 \sqrt{c}. \quad . \quad . \quad . \quad . \quad (15)$$

TABLE X.

Activity Coefficients of HCl in Ethyl Alcohol at round concentrations.

C.	f smoothed.	Milner.		Debye.		f calc., eqn. 15.	$\dfrac{\Lambda_c}{\Lambda_0}$.
		$f(c)$.	f, eqn. 9.	f, eqn. 6.	f, eqn. 6a.		
0·0001	0·955	0·710	0·954	0·937	0·940	0·957	0·960
·0002	·938	·700	·937	·912	·918	·941	·946
·0005	·905	·688	·903	·865	·879	·908	·912
·001	·870	·680	·868	·814	·840	·872	·876
·002	·823	·673	·820	·748	·796	·824	·826
·005	·737	·661	·734	·632	(·737)	·736	·731
·01	·654	·647	·652	·523	·713	·648	·658
·02	·555	·628	·556	·399	·744	·542	·580
·05	·434	(·61)	·412	·234	...	·380	·485

It is interesting to note, as we pass from solutions in water to solutions in the ethyl alcohol, how the conductivity ratio approaches the activity coefficient, suggesting that in ethyl

* McKelvy, Bull. Bur. Standards, ix. p. 327 (1913).
† Journ. Chem. Soc. ciii. p. 252 (1913).
‡ Zeits. Phys. Chem. lxxxix. p. 131 (1915).

alcohol and in solvents of lower dielectric constant, the law of mass action might appear to be obeyed by fairly strong electrolytes. 'Molal' activity coefficients γ are given in Table VI.

Discussion.

Although in dilute solutions E_0 (Milner) is not quite constant within the experimental error, it is none the less obvious that Milner's equation for $\log f$ is so nearly obeyed that it serves as an accurate extrapolation formula for the determination of E_0, which Debye's equation does not. In fact, Debye's factor A is in error by an amount which cannot be corrected for even by assuming absurdly large values for B (and therefore for the ionic radius), but only by a fraction given approximately by $f(c)$, which is variable with the concentration and also with the solvent. At 0.0005 N, $f(c)$ has the values 0.727, 0.70, and 0.69 in the three solvents water, methyl and ethyl alcohols; whereas the ratio of the empirical A′ of equations (14), (12), and (15) to Debye's A is 0.724, 0.70, and 0.67 respectively—a fairly close agreement.

We have already referred to the paper by Pike and Nonhebel, in which it is shown that probably neither the equation of Debye nor that of Milner can do more than predict the general shape of the curve $-\log f / c$. Since Debye's theory gives $-\log f \propto c^{0.5}$ and Milner's $-\log f \propto c^{0.487}$ approximately, it is impossible to discriminate with certainty between the two theories without much more precise and numerous measurements. The shape of the curve shown in fig. 3 and the empirical equations (14), (12), and (15) seem to be more in favour of the square root relation, while Lewis and Linhart appear to think that the exponent of c is, if anything, somewhat greater than 0.5 (see Lewis and Randall, 'Thermodynamics,' p. 344, table i.).

The Relation between the Activities of Electrolytes in Different Solvents, and the Free Energy of Transfer of Hydrogen Chloride from Alcoholic to Aqueous Solutions.

The E.M.F. E_5 of a cell of the type

$$\text{Ag}: \text{AgCl} / \text{HCl in alcohol} / \overset{\frown}{\text{H}_2 / \text{H}_2} / \text{HCl in water} / \text{AgCl}: \text{Ag}$$
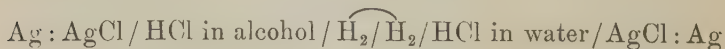
is a measure of the free energy decrease when one mol of hydrogen chloride is transferred isothermally and reversibly from a solution in alcohol of activity a_3 to an aqueous solution of activity a_4. Table XI. illustrates the magnitude of this quantity when one mol of hydrogen chloride is transferred from a solution in alcohol to a solution of equal molal

TABLE XI.

Free Energy of Transfer of HCl from Alcohols to Water.

M in both solutions.	Calories.	
	$-\Delta F_{\mathrm{W-MeOH.}}$	$-\Delta F_{\mathrm{W-EtOH.}}$
0·001	5256	.....
·01	5076	5831
·1	4670	5298
·5	4253	4795
1·0	...	4435
2 0	...	4040
Activities equal.	5619	6473

concentration in water, the value of the volt-faraday being taken as 23074 calories. Now it is important to remember that, owing to the choice of a different standard state for each solvent, the E.M.F. E_5 of such a cell is not given by the expression for a simple concentration cell without a liquid junction, *i. e.* by equation (4), but by the equation :

$$E_5 = (E_4{}^0 - E_3{}^0) - \frac{2\mathrm{RT}}{\mathbf{F}} \ln \frac{a^{\mathrm{H_2O}}}{a^{\mathrm{alc.}}}$$

$$= E_5{}^0 - \frac{\mathrm{RT}}{\mathbf{F}} \ln \frac{a_2{}^{\mathrm{H_2O}}}{a_2{}^{\mathrm{alc.}}}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (16)$$

where a_2 is the activity of the undissociated solute. Hence, when the activity of the electrolyte in each solution is the same, *e. g.* at infinite dilution,

$$-\Delta F = 23074\,(E_w{}^0 - E_{\mathrm{alc.}}{}^0) = 23074\,E_5{}^0.$$

The large influence of traces of water on the activity of hydrogen chloride in alcoholic solutions is worthy of note in relation to the figures in the table.

Owing to the omission of this E_5^0 term, the activity co-efficients of lithium chloride given by Pearce and Hart [*] are only relative and have not the same thermodynamical significance as those defined by Lewis.

Activity and Vapour Pressure.

The value of E_5^0 enables us to calculate the equilibrium constant for the reaction taking place in the two-solvent cell, *i. e.* for the transfer of hydrogen chloride from one solvent to the other.

If
$$K = \frac{a_2'^{\;H_2O}}{a_2'^{\;alc.}},$$

where $a_2'^{\;H_2O}$ and $a_2'^{\;alc.}$ are the activities which are in equilibrium in the two-solvent cell, then when the electrolyte is present in its standard state in each solvent,

$$-\Delta F^0 = 23074 \, E_5^{\circ} = RT \ln K,$$

whence K has the value 13,030 for the system methyl alcohol–water and 55,000 for the system ethyl alcohol–water.   Hence, in order that there may be no tendency for the hydrogen chloride to pass from one solution to the other, the activity of the undissociated portion must be K times greater in the aqueous than in the alcoholic solution.   Knowing the value of K, we can calculate the partial pressure of the hydrogen chloride over its alcoholic solutions if its partial pressure over one aqueous solution is known.   For

$$a_2^{H_2O} = k_1 P_{HCl}^{H_2O} \quad \text{and} \quad a_2^{alc.} = k_2 P_{HCl}^{alc.}.$$

But for equilibrium $\quad P_{HCl}^{H_2O} = P_{HCl}^{alc.}, \qquad$ whence $K = \dfrac{k_1}{k_2}.$

k_1 can be obtained from the measurements of Dunn and Rideal [†] and the values in Table VIII.; if P is expressed in mm. of mercury, its average value is 2200. Hence k_2 (methyl alcohol)$=0.169$ and P_{HCl} for a 0.4802 M solution has the value 0.083 mm.   The partial pressure of this solution has been measured by H. G. Smith in this laboratory, using the method and apparatus of Bates and Kirschmann [‡]. As a result of two concordant determinations, he found $P_{HCl} = 0.084 \pm .003$ mm., which agrees well with the value calculated from the E.M.F. measurements.

For solutions in ethyl alcohol, $k_2 = 0.04$.   Jones and

[*] Journ. Amer. Chem. Soc. xliv. p. 2411 (1922).

[†] Journ. Chem. Soc. cxxvi. p. 677 (1924).

[‡] Journ. Amer. Chem. Soc. xli. p. 1991 (1919).

Lapworth * have measured the partial pressure of hydrogen chloride over its solutions in ethyl alcohol ; the calculated and observed values are shown in Table XII. The agreement is bad, due in part, no doubt, to the paucity of the electromotive force measurements, from which the activity coefficients of the hydrogen chloride were obtained.

TABLE XII.

M.	P_{HCl} obs.	P_{HCl} calc.
0·3518	0·108 mm.	0·131 mm.
0·9641	0·417	0·489
1·511	0·811	1·04
3·151	2·63	4·07

Summary.

1. The activity coefficients and transport numbers of solutions of hydrogen chloride in methyl alcohol have been obtained by measurements of electromotive force.

2. It has been shown that the activity coefficients of hydrogen chloride in the three solvents, water, methyl and ethyl alcohols agree fairly well with those calculated from Milner's equation for the interionic electrical energy in a solution of a completely dissociated electrolyte, but do not agree with those calculated from Debye's equations.

3. The relation between the activities of electrolytes in different solvents has been pointed out, and it has been shown how the partial pressure of hydrogen chloride over its solutions in one solvent may be calculated from its vapour pressure over a second solvent and a series of E M.F. measurements in both solvents.

In conclusion, we wish to express our thanks to Mr. J. W. Woolcock for assistance in some of the experimental work, to the Chemical Society for a grant which has defrayed part of the cost of this investigation, and to the Advisory Council of the Board of Scientific and Industrial Research for a maintenance grant to one of us (G. N.) which has enabled this work to be concluded.

Physical Chemistry Laboratory,
    Balliol College and Trinity College,
                    Oxford.
            May 1925.

* Journ. Chem. Soc. ciii. p. 252 (1913).

LXXX. *Regeneration in Tuned Three-element Vacuum-tube Circuits.* By EDWARD H. LANGE, *Assistant Professor of Electrical Engineering and Physics, Post-graduate School, U.S. Naval Academy* *.

THE regenerative action, amplification, and stability of a three-element vacuum-tube in connexion with tuned circuits can be determined for a number of typical circuits by a simple graphical method. In this paper, only the first-order effects resulting from a linear relation between current and e.m.f. are considered, but the method is also useful where non-linear relations exist. The circuits considered are shown in figs. 1, 2, 3, and 4. In each case an alternating signal voltage E'_{gs} is assumed to be set up in the grid coil by inductive coupling, and the vacuum-tube circuit to be tuned to the signal frequency. It is necessary to distinguish between the applied signal voltage E'_{gs}, the voltage drop E_{gs} across the grid coil when there is no regeneration, and the e.m.f. E_g set up in the grid coil due to regeneration. E_{gs} will be larger than E'_{gs}, due to voltage amplification when the grid coil is part of a resonant circuit, as in figs. 2, 3, and 4.

Fig. 1.
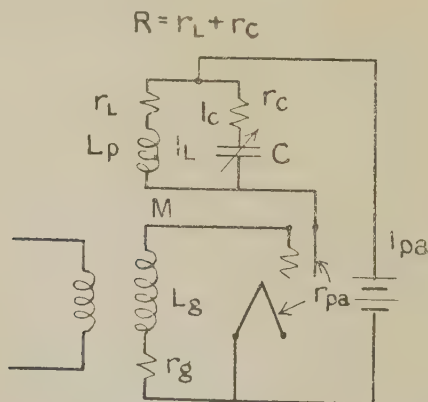
Considering first the circuit in fig. 1, the alternating current I_{pa} in the plate circuit is

$$I_{pa} = \frac{\mu E_{gs}}{r_{pa} + r_{eq}}, \quad \cdots \quad (1)$$

where μ is the voltage simplification factor, r_{pa} the

* Communicated by the Author.

alternating-current resistance of the tube between plate and filament, and r_{eq} the equivalent resistance at resonance of the parallel circuit. In terms of the inductance L, capacity C, and total resistance R of the parallel circuit branches the equivalent resistance is

$$r_{eq} = \frac{L}{RC}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Fig. 2.
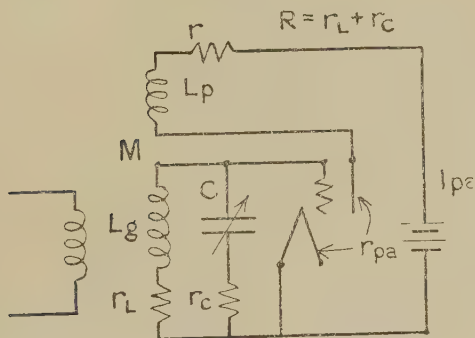
Fig. 3.
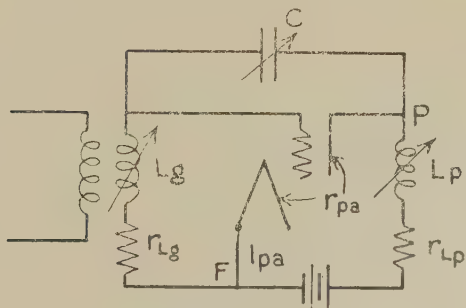
When there is no coupling between the grid and plate coils, equation (1) gives the alternating plate current corresponding to the impressed signal voltage $E'_{gs} = E_{gs}$. If, now, the grid and plate coils are coupled with a mutual inductance M, the alternating e.m.f. set up in the grid coil due to the current I_L in the inductive branch of the plate circuit is

$$E_g = \omega M I_L, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$\omega = 2\pi f = \frac{1}{\sqrt{LC}}. \quad . \quad . \quad . \quad (4)$$

The current amplification of the parallel circuit at resonance, in terms of the circuit constants, is

$$\alpha = \frac{I_L}{I_{pa}} = \frac{1}{R}\sqrt{\frac{L}{C}}. \quad . \quad . \quad . \quad . \quad (5)$$

From (3), (4), and (5),

$$E_g = \frac{M}{RC} I_{pa}. \quad . \quad . \quad . \quad . \quad (6)$$

Fig. 4.
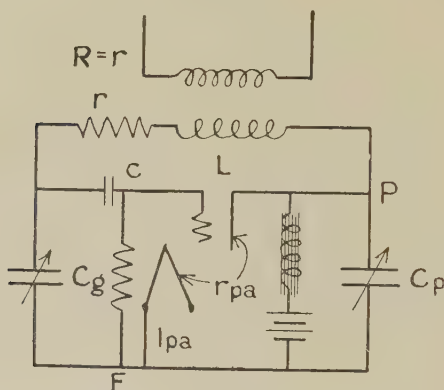
Fig. 5.
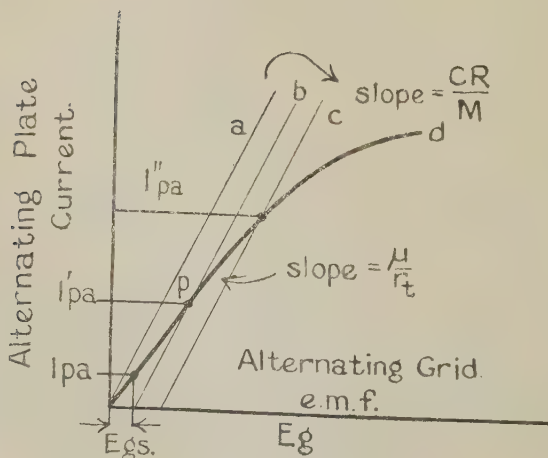
This e.m.f. will be in phase with the signal e.m.f. E_{gs} (or have a 180° phase-angle if one coil is reversed), provided the reactance-resistance ratio of the parallel circuit

is sufficiently high. Equation (1) is the dynamic characteristic of the tube : it gives the grid e.m.f. required to produce a specified plate current ; equation (6) gives the grid e.m.f. obtained for the same value of plate current. Referring to fig. 5, the curve *d* is the dynamic characteristic ; the curve has a constant slope for a considerable portion defined by the dynamic mutual conductance

$$\frac{I_{pa}}{E_{gs}} = \frac{\mu}{r_{pa} + r_{eq}} = \frac{\mu}{r_t'}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

where r_t is the total alternating plate-circuit resistance.

Fig. 6.
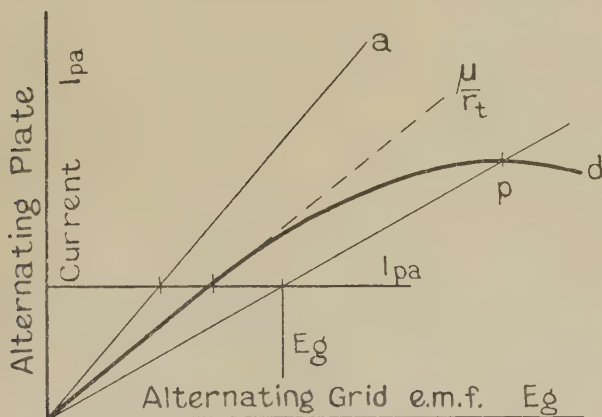
From equation (6) the regenerative e.m.f. E_g is also related to the plate current I_{pa}, the relation being shown by curve *a* (fig. 5). The slope of curve *a* in accordance with equation (6) is

$$\frac{I_{pa}}{E_g} = \frac{RC}{M}.$$

When there is no regeneration, *i. e.* when $M = 0$, the signal e.m.f. produces the plate current I_{pa}. For a definite coupling M, the horizontal line I_{pa} intersects the curve *a* and gives the corresponding regenerative e.m.f. E_g. The total e.m.f. impressed on the grid is therefore $E_{gs} + E_g$. With this increased grid voltage the plate current will not remain constant at its original value, but increases along the curve *b* drawn parallel to *a* until the point *p* is reached. The plate current at *p* is I'_{pa}, and it remains stationary at this point as long as the signal e.m.f. E_{gs} is

constant. A current greater than I'_{pa} would not give sufficient regenerative e.m.f. together with the signal e.m.f. to be maintained in accordance with the dynamic characteristic. If the impressed signal is doubled, the plate current increases until the curve c drawn parallel to a intersects the dynamic characteristic. The new value of plate current is then $I''_{pa} = 2I'_{pa}$, provided the straight portion of the dynamic characteristic has not been exceeded. Thus, so long as the slope of the dynamic characteristic is less than $\dfrac{RC}{M}$, self-sustained oscillations will be produced which are under the control of the impressed signal e.m.f., and which result in amplification of the plate current. With no impressed signal e.m.f. no self-sustained oscillations will be produced, since the curve a intersects the dynamic characteristic at zero plate current. As the value of M is increased, the slope of the lines a, b, c is decreased, giving greater signal amplification. The regenerative amplification ratio is

$$\rho = \frac{I'_{pa}}{I_{pa}} = \frac{E_{gs} + E_g}{E_{gs}}, \quad \ldots \quad \ldots \quad (8)$$

or the absolute amplification is

$$\rho_0 = \rho - 1 = \frac{E_g}{E_{gs}};$$

and from (6) and (7)

$$I'_{pa} = \frac{\mu}{r_t}(E_{gs} + E_g) = \frac{RC}{M}E$$

Therefore

$$\rho_0 = \frac{\dfrac{\mu}{r_t}}{\dfrac{RC}{M} - \dfrac{\mu}{r_t}}. \quad \ldots \quad \ldots \quad (9)$$

The amplification due to regeneration can be made infinite, as indicated by (9), but to obtain large amplification of a very small signal implies practical coincidence of the curve a and the dynamic characteristic (fig. 5). This coincidence is indicated by a zero value of the denominator in equation (9).

When $\dfrac{RC}{M} = \dfrac{\mu}{r_t}$, self-sustained oscilllations are produced which are no longer under the control of the impressed signal voltage. The stability of regeneration is therefore measured by $1/\rho_0$.

When $\dfrac{RC}{M}$ is definitely less than $\dfrac{\mu}{r_t}$, the slope of the

curve *a* (fig. 6) is less than the initial slope of the dynamic characteristic; but, due to the fact that the slope of the dynamic characteristic decreases for larger values of plate current, the two curves intersect at the point *p* (fig. 6). For any current I_{pa} shown by the horizontal line and less than current at *p*, the regenerative e.m.f. E_g will be greater than is necessary to maintain the current I_{pa}, so that the plate current increases until the point *p* is reached. The magnitude of the alternating plate current for self-sustained oscillations and any value of coupling M is therefore fixed by the intersection *p*.

The equivalent resistance of the external plate circuit of fig. 1 is independent of the coupling when the grid current is considered negligible and the regenerative e.m.f. increases continuously with the coupling. For the circuit shown in fig. 2 a different condition prevails. The dynamic mutual conductance is given by equation (7) for each of the circuits considered; the value of r_{eq}, however, depends upon the external resonant circuit. For fig. 2, if R is the resistance of the grid circuit, and *r* the resistance of the external plate circuit,

$$r_{eq} = r + \frac{\omega^2 M^2}{R}.$$

At resonance $\omega^2 = \dfrac{1}{L_g C}$ practically; and since the resistance *r* is ordinarily negligible compared with the alternating current resistance of the tube

$$r_{eq} = \frac{\omega^2 M^2}{R} = \frac{M^2}{L_g C R}; \quad . \quad . \quad . \quad . \quad (10)$$

therefore

$$r_t = r_{pa} + \frac{M^2}{L_g C R}; \quad . \quad . \quad . \quad . \quad (11)$$

The value of ω used above is not identical with the value which makes the power factor of the plate-circuit unity, but differs from it by a negligible quantity. Also the reactance of the plate circuit is ordinarily negligible for the resonant condition compared with the total plate-circuit resistance r_t. The voltage amplification of the resonant grid circuit is

$$\alpha = \frac{1}{R} \sqrt{\frac{L_g}{C}}. \quad . \quad . \quad . \quad . \quad (12)$$

For an impressed signal e.m.f. E'_{gs}, the voltage applied between grid and filament without regeneration is

$$E_{gs} = \alpha E'_{gs}. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

When the grid and plate circuits are coupled with a mutual inductance M, the regenerative e.m.f. is

$$E'_g = \omega M I_{pa} = \frac{M}{\sqrt{L_g C_g}} I_{pa},$$

and the regenerative e.m.f. applied to the grid is

$$E_g = \alpha E'_g = \frac{M}{C_g R} I_{pa}$$

or

$$\frac{I_{pa}}{E_g} = \frac{R C_g}{M}. \qquad \qquad (15)$$

For a large resistance-reactance ratio of the plate circuit and small resistance-reactance ratio of the grid circuit, the e.m.f. E_g applied to the grid is practically in phase with the plate current (or has a phase-angle of $180°$ if one coil is reversed. Equations (7) and (15) determine the action of the circuit in amplifying the impressed signal, as in the case of circuit 1 : however, since the total plate-circuit resistance r_t increases when the coupling is increased, the initial slope of the dynamic characteristic d decreases along with the slope of curves a, b, c, etc. (fig. 5).

The alternating current in the plate circuit, due to a signal voltage E'_{gs} and corresponding impressed grid voltage $\alpha E'_{gs} = E_{gs}$ when $M = 0$, is

$$I_{pa} = \frac{\mu E_{gs}}{r_{pa}}, \qquad \qquad (16)$$

since the equivalent resistance in the plate circuit of the tuned grid circuit is zero, and the impedance of the plate coil is considered small compared with the tube resistance. For any coupling M, the amplified plate current I'_{pa} (fig. 5) will reach an equilibrium value at p, where the curves b, c, etc. intersect the dynamic characteristic, which has a different slope for each value of M. For the equilibrium condition, from equations (7) and (15),

$$I'_{pa} = E_g \frac{R C_g}{M} = \frac{\mu (E_g + E_{gs})}{r_t}. \qquad \qquad (17)$$

The amplification ratio is therefore

$$\rho = \frac{I'_{pa}}{I_{pa}} = \frac{r_{pa}}{r_t} \cdot \frac{\dfrac{R C_g}{M}}{\dfrac{R C_g}{M} - \dfrac{\mu}{r_t}}. \qquad \qquad (18)$$

The circuit 2 therefore functions as an oscillator under the control of the impressed signal as long as the curves a, b, c, etc. have a slope definitely greater than the slope of the dynamic characteristic as the coupling is increased. When $\frac{RC_g}{M} < \frac{\mu}{r_t}$, self-sustained oscillations which are no longer under control of the impressed signal are produced. Increasing the coupling M within certain limits gives an increased magnitude of self-sustained oscillations in accordance with fig. 6; but since the plate-circuit resistance r_t increases by an amount proportional to the change in M^2, a condition is ultimately reached where the slope of the dynamic characteristic is decreasing faster than the slopes of a, b, c, etc. as M increases, and the point of intersection p recedes to zero. The upper and lower limits of M when the system acts as an oscillator are given by the relation

$$\frac{RC_g}{M} < \frac{\mu}{r_t} = \frac{\mu}{r_{pa} + \dfrac{M^2}{L_g C_g R}}. \quad . \quad . \quad . \quad . \quad (19)$$

Considering next the circuit arrangement of fig. 3, or the Hartley circuit, the system consists of a parallel resonant circuit across the points PF, one branch having an inductance L_p and resistance r_{Lp}, the other branch having a capacity C, inductance L_g, and resistance r_{Lg} in series. For parallel-circuit resonance the resultant reaction of the grid branch must be capacitive, since the plate branch is always inductive. Neglecting the effect of the branch resistances, the resonant frequency for the parallel circuit is the same as the resonant frequency of the series circuit formed by the two branches and consisting of L_p, L_g, and C in series.

Thus

$$\omega = 2\pi f = \frac{1}{\sqrt{(L_p + L_g)C}}, \quad . \quad . \quad . \quad (20)$$

and the equivalent resistance at resonance is

$$r_{eq} = \frac{L_p^2}{(L_p + L_g)RC}. \quad . \quad . \quad . \quad (21)$$

The dynamic mutual conductance is given by equation (7), where the value of r_{eq} is that of equation (21), and the effect on the initial slope of the dynamic characteristic of a

variation in L_p or L_g is indicated by (21). The parallel-circuit current amplification at resonance is

$$\alpha = \frac{L_p}{\sqrt{(L_p + L_g)C} \cdot R} \qquad . \quad . \quad . \quad (22)$$

A current I_g in the grid branch produces a voltage drop from grid to filament of magnitude

$$E_g = \omega L_g I_g = \omega L_g \alpha I_{pa}.$$

Therefore

$$\frac{I_{pa}}{E_g} = \frac{L_p + L_g}{L_p} \cdot \frac{RC}{L_g} \cdot \quad . \quad . \quad . \quad . \quad (23)$$

Let $L_p + L_g = L$ and $L_g < L$.

If the grid and plate inductances are simultaneously varied to keep the circuit tuned, L will be constant. Then

$$\frac{I_{pa}}{E_g} = \frac{LRC}{LL_g - L_g{}^2}.$$

As L_g is increased, the slope of the lines a, b, c, etc. (fig. 5) given by equation (23) at first decreases until $L_g = L_p$, after which it again increases. Also, as L_g is increased keeping L constant, the equivalent resistance decreases, thereby increasing the initial slope of the dynamic characteristic. In this respect circuit (3) performs the reverse of circuit (2). Increasing L_g to increase the regenerative e.m.f., tends to approach the unstable condition more rapidly than a corresponding change in circuits (1) or (2), because of the double action on the regenerative e.m.f. and dynamic characteristic tending to make the lines parallel. The equilibrium-tube plate current I'_{pa}, due to the superposition of the impressed signal E_{gs} and regenerative e.m.f. E_g under control of E_{gs}, is given by equations (7) and (23.

Thus

$$I'_{pa} = E_g \frac{L_p + L_g}{L_p} \cdot \frac{RC}{L_g} = \frac{\mu(E_g + E_{gs})}{r_t} . \quad . \quad (24)$$

The regenerative grid-voltage amplification ratio is therefore

$$\rho = \frac{E_g + E_{gs}}{E_{gs}} = \frac{\beta RC}{\beta RC - \dfrac{\mu}{r_t}}, \qquad . \quad . \quad (25)$$

where $\beta = \dfrac{L_p + L_g}{L_p L_g}.$

As L_g is increased, keeping the circuit tuned, the amplification ratio approaches infinity. The condition for self-sustained oscillations not controlled by the impressed signal is therefore

$$\frac{L_p + L_g}{L_p L_g} \cdot RC \le \frac{\mu}{r_t} = \frac{\mu}{r_{pa} + \dfrac{L_p{}^2}{(L_p + L_g)RC}}. \quad . \quad (26)$$

In fig. 4 is shown the Colpitts circuit. The plate is energized through a reactance coil which carries the continuous current component of the plate current. In order to keep the steady plate potential from the grid, a condenser c and leak resistance are used. The effect of this connexion is to increase somewhat the apparent resistance r and capacity C_g of the resonant circuit. Considering the external circuit as a parallel circuit across the tube resistance r_{pa}, *i.e.* between P and F, one branch contains the capacity C_p and the other L, C_g, and r in series. The resonant frequency, neglecting the effect of resistance, for either the parallel circuit or the series circuit formed by the two branches is given by

$$\omega = 2\pi f = \sqrt{\frac{1}{L}\left(\frac{1}{C_g} + \frac{1}{C_p}\right)}. \quad . \quad . \quad . \quad (27)$$

The equivalent resistance at resonance of the parallel resonant circuit is

$$r_{eq} = \frac{L}{RC_p} \cdot \frac{C_g}{C_p + C_g}. \quad . \quad . \quad . \quad (28)$$

and the current amplification in the parallel circuit at resonance is

$$\alpha = \frac{1}{R}\sqrt{\frac{L}{C_p}} \cdot \sqrt{\frac{C_g}{C_p + C_g}}. \quad . \quad (29)$$

For a branch current I_g in the grid circuit, the voltage applied to the grid is

$$E_g = \frac{I_g}{\omega C_g} = \frac{\alpha I_{pa}}{\omega C_g}$$

or

$$\frac{I_{pa}}{E_g} = \frac{(C_p + C_g)R}{L}. \quad . \quad . \quad . \quad . \quad (30)$$

Equation (30) determines the slope of the lines a, b, c, etc. (fig. 5) for the Colpitts circuit. The initial slope of the dynamic characteristic is determined by equation (7), for which the appropriate value of r_{eq} is given by equation (28). For a large reactance-resistance ratio of the tuned circuit, the voltage drop E_g across the grid condenser sets up in the

plate circuit an e.m.f. μE_g in phase with the driving e.m.f. of the plate circuit necessary to maintain the alternating current I_{pa}.

If the circuit is kept tuned as C_g and C_p are varied, the resultant capacity of C_g and C_p in series must be constant. Calling C the resultant capacity,

$$C = \frac{C_p C_g}{C_p + C_g}. \quad \quad \quad \text{. . . . . . . (31)}$$

From (30) and (31),

$$\frac{I_{p,\imath}}{E_g} = \frac{C_g C_p}{C} \cdot \frac{R}{L} = \frac{C_g{}^2}{C_g - C} \cdot \frac{R}{L} \quad \text{. . . (32)}$$

and $\quad C_g > C.$

For large values of C_g the grid to filament voltage drop is small, *i.e.* very little regenerative e.m.f. is applied to the grid, and the slope of the lines *a*, *b*, *c* (fig. 5) is large. As C_g is decreased, the slope decreases until $C_p = C_g$, after which a further decrease of C_g increases the slope of the lines *a*, *b*, *c*, etc. Also, as the regeneration is increased by decreasing C_g, the equivalent resistance decreases, thereby increasing the initial slope of the dynamic characteristic. The equilibrium current I_{pa} corresponding to the intersection of the lines *b*, *c*, etc. (fig. 5) is

$$I'_{pa} = E_g \frac{C_g + C_p}{L} \cdot R = \frac{\mu(E_g + E_{gs})}{r_t}.$$

The regenerative amplification ratio of the grid voltage is

$$\rho = \frac{E_g + E_{gs}}{E_{gs}} = \frac{\dfrac{C_p + C_g}{L} \cdot R}{\dfrac{C_p + C_g}{L} \cdot R - \dfrac{\mu}{r_t}}. \quad \text{. . . . (32)}$$

From (32) the condition for self-sustained oscillations is

$$\frac{C_p + C_g}{L} \cdot R \leqq \frac{\mu}{r_t} = \frac{\mu}{r_{pa} + \dfrac{L}{C_p R} \cdot \dfrac{C_g}{C_p + C_g}}. \quad \text{. . . (33)}$$

In each of the circuits considered, the coupling used for increasing the signal e.m.f. on the grid has been assumed sufficiently loose that the reaction of the regenerative tube circuits on the signal circuit can be neglected. Although the several circuits have been considered separately, the regeneration of circuit 3 will in general influence the regeneration of circuits of forms 1 and 2 due to inter-electrode capacity.

LXXXI. *Fine Structure, Absorption, and Zeeman Effect of the* 2536 *Mercury Line. By* R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University* *.

[Plate XXIV.]

A PRELIMINARY study of the fine structure of the 2536 line of mercury was made last year in connexion with the study of the optical excitation of the vapour of the metal *in vacuo* and at room temperature, by the light from a water-cooled quartz mercury arc. It was found possible to control the orbital transfers of the electrons by simultaneously illuminating the vapour with light of two or more selected frequencies obtained in some cases from the same lamp, and in others from two lamps each furnished with appropriate ray filters. A preliminary account of the work was published in the Proceedings of the Royal Society, vol. 106, p. 679, under the title "Controlled Orbital Transfers of Electrons in Optically Excited Mercury Vapour." Continuation of the work, in which the effect has been increased in intensity about eightfold, by employing a magnetic field to press the discharge against the tube-wall, has shown that the intensity ratios of the lines emitted by the vapour are affected in a most remarkable manner by the action of the magnetic field on the exciting light.

As all of the phenomena have their origin in the absorption of the light of the 2536 line by the vapour, by which the electrons are raised from the $1S$ to the $2p_2$ orbit, from which they are raised to higher levels by the absorption of light of other wave-lengths, it is a matter of the utmost importance to secure all possible data regarding the line in question.

Nagaoka has published recently a very comprehensive monograph on the fine structure of the mercury lines illustrated with very beautiful photographs made with two crossed Lummer-Gehrke plates of quartz. Finding that his results for the 2536 line could not very well be reconciled with those which I had previously obtained with a single quartz plate, I commenced the study of the line with more powerful apparatus. The plate which I employed in the earlier investigation was crossed with a very fine one recently secured from the firm of Adam Hilger, which they state is made from the most perfect crystal of quartz that has ever come into their possession. The plate measures $200 \times 30 \times 5$ mm. with a prism for the entrance of the light at the proper angle attached by the "optical contact" method introduced by the

Hilger Company. Aside from its transparency in the ultra-
violet, the quartz interference-plate has the advantage of
being made from an optically homogeneous medium, far
superior to even the best optical glass, and I find it much
more convenient, as an instrument for the study of line
structure, than the echelon.

The technique of working with these plates in the ultra-
violet region is a little involved, and as I was unable to
find anything pertinent in the literature, and spent some
little time in learning how to use the instrument for this
purpose, a few hints on the subject may be of use to others
beginning work along these lines.

In the first place we must use polarized light, since the
quartz is doubly refracting and yields two superposed inter-
ference patterns if used with unpolarized radiations. A
quartz Rochon prism, cemented with glycerine, is suitable as
a polarizer, and it is best to use the image in which the
electric vector is parallel to the surface of the plate, on
account of the higher reflecting power of the plate for this
component. There are two ways in which the double-image
prism can be used, one of them involving the use of a lens
of fused quartz, the other not. We will begin with the
latter.

Taking as our source of light a water-cooled quartz mercury
arc, the most suitable type being the simple vertical burner
with an anode of tungsten and the cathode bulb immersed
in running water to a depth of about 1 cm. above the con-
striction, we mount the interferometer plate (horizontal) at
a distance of about a metre from the arc and place the
Rochon prism midway between the two. The prism should
be mounted at the centre of a large opaque screen in such
a position that the two images appear side by side, one
polarized vertically the other horizontally. If now we view
the two images through the plate, holding the eye a trifle
above the plane of its upper surface, we see at once the
multiple images formed by the emergent ray-bundles, as
two series of narrow superposed horizontal slits, the number
of slit images being greater in the image polarized with its
electric vector horizontal. It may be necessary to raise or
lower the end of the plate nearest the eye to bring the images
into view, since the vertical height of the source is limited
by the Rochon prism. The plate in this position is not
transmitting any light of wave-length 2536, as we shall see
presently, and we must next familiarize ourselves with its
behaviour. If we lower the end nearest the eye the images
eventually become red, all of the other colours being incident

on the inner surfaces at angles exceeding the critical angle, and hence totally reflected within the plate.

The Rochon prism may be placed close to the quartz interferometer plate, in which case the vertical height of the source becomes equal to the full height of the lamp and a wider range of wave-lengths are transmitted by the plate in a given position. If the end of the plate nearest the eye is raised the images seen at grazing emergence become violet in colour. If, with the plate in this position, we form the images of the fringes on the wide open slit of a quartz spectrograph by means of a quartz lens, and photograph the fringes in the spectrum lines, we shall probably find that **no** trace of the 2536 line appears. This is because the rays are totally reflected within the plate, as mentioned above. To bring the line into view we shall have to raise the end of the plate a little further, and if the vertical height of the source is small it may happen that the 2536 line is the only one which appears on the plate. It may be argued that all of this explanation is unnecessary, since, by bringing the source nearer the quartz plate, we can have all of the lines transmitted. This of course is true with a single plate, but when two plates are used simultaneously in the crossed position, it is the width of the source which is effective in transmitting a wide range of wave-lengths, and we cannot make this very large as we are obliged to use a *narrow* vertical source in order to get complete separation of the images by the Rochon prism.

We will now take the case of the two crossed plates. The first plate we will consider in the horizontal position with its auxiliary prism below. The second plate is mounted close to the first pointing down at its upper surface at a very small angle, so that the rays leaving the first plate near the grazing angle enter the auxiliary prism of the second plate, which we will suppose to be on our right as we face the source. The second plate must be so pointed that it receives the light from the image in the Rochon prism in which the electric vector is horizontal, which we will suppose is the right-hand image as we face the lamp. (This will be the image which is transmitted by a nicol prism with its short diagonal in the horizontal position.) The vibrations in this beam are of course not properly oriented for most efficient transmission through the second plate. For the best results a quartz plate, cut perpendicular to the axis, and of such thickness that it will rotate the plane of polarization an odd multiple of 90° for light of the desired wave-length, should be mounted between the two interferometers. This refinement, however, I dispensed with and found that fairly

sharp interference dots were obtained without employing it.
A quartz lens of about 30 cm. focus is next mounted close to
the second plate and the slit of the spectrograph brought up
into the interference pattern at its focal plane.   On bringing
the eye into the position of the photographic plate we adjust
the instrument, by raising or lowering its feet with blocks or
fragments of glass, until the brilliant spot of light is at the
centre of the iris diaphragm.   The slit should be opened to
a width of one or two millimetres.   We now examine the
pattern of the interference dots in the green line with a
short-focus lens, adjusting the plates in such a way that the
dots form a square pattern, with say four or five dots in the
vertical rows.   We may have to raise or lower the quartz
lens, which should be mounted at the end of a tube forming
a telescope without an eyepiece.   It is a good plan to learn
how to photograph the fringes formed by a single plate before
trying to operate two plates.   The spectrograph and quartz
lens are so adjusted that the green line is traversed by four
or five horizontal fringes.   This means simply that one end
of the slit is very near the edge of the interference pattern
where the fringes are far apart.   The end of the quartz plate
nearest the lens is now raised until the green line disappears,
the violet line remaining.   If the 2536 line does not appear
in the photograph, we elevate the end of the plate by degrees
until it comes into view.   With only four or five fringes in
the green line we shall find a dozen or more in the ultra-
violet line.

With two plates crossed, we perform the above routine
twice.   Starting where we were a moment ago, with the
green dots visible in the focal plane of the spectrograph,
we slip pieces of thin glass under the foot of the first plate,
abolishing first the green and then the violet line.   The first
plate is now probably transmitting the 2536 line, but as
no visible light gets through, we have no means of adjusting
the second plate.   To do this we remove the glass plates
from under the foot of the first plate, and then rotate the
second plate in a clockwise direction until the green line
disappears, the violet remaining : a further rotation of about
one degree will bring the plate into the correct position,
and we now replace the glass plates and make a trial
exposure.

Another disposition of the apparatus may be employed if a
lens of fused quartz is available.   The light from the lamp is
rendered parallel by a lens of crystal quartz, passed through
the Rochon prism and focussed on the prism of the Lummer-
Gehrke plate by the fused quartz lens, one of the two

polarized images being intercepted by a screen. It is important to remember in all work with polarized light that a lens of crystal quartz, cut perpendicular to the axis, rotates the plane of polarization of the transmitted rays in varying amounts, depending upon the thickness of quartz traversed.

This disposition was used in the latter part of the work, and was found preferable in some respects to the other arrangement. It is possible to dispense with the polarizing prism entirely, getting rid of one of the two sets of fringes by proper inclination of the plate. This requires a rather small source of light.

The Mercury Lamps.

Lamps of three different types were employed in the present investigation.

1. A commercial Cooper-Hewitt quartz mercury arc of the vertical type with a tungsten anode and mercury cathode.

Fig. 1.
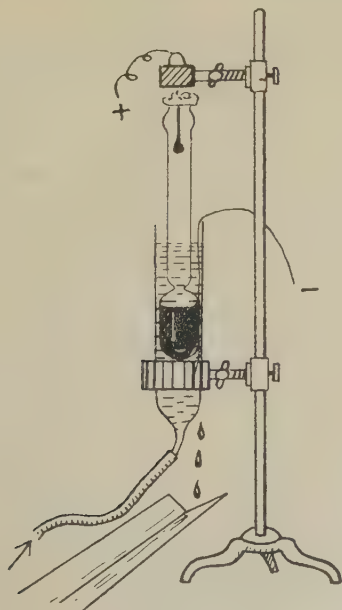
The cathode bulb was immersed in running water which came up to a point about 1 cm. above the constriction. The lamp was supported by a clamp which gripped the anode terminal, and the water-cell held by another clamp, both being attached to the same iron stand, as shown in fig. 1.

This arrangement enables one to tilt the lamp for ignition without removing it from the water, by simply tilting the iron stand on two of its three feet. The rate of water flow was about three drops per second, the overflow being carried off to a sink by a tin gutter.

The arc was operated with a 110 volt current with sufficient ohmic resistance to keep the current down to about 1·5 amperes, a large self-inductance coil being included in the circuit to keep the lamp from going out. The potential drop across the poles of the lamp was from 18 to 20 volts. Included in the circuit was a large helix with a core of soft-iron wires 5 cm. in diameter and 40 cm. long, the end of which was brought up to within a distance of about 7 cm. from the tube of the quartz arc. The magnetic field pressed the discharge against the wall of the lamp on the side towards the interferometer, and prevented the reversal of the components of the line, which occurs when the lamp operates normally. As this type of lamp is best suited for the study of all phenomena involving the use of the 2536 line, such as polarized resonance radiation and the optical excitation of other lines, it may be well at this point to draw attention to certain peculiarities regarding the emission of this radiation which, if not allowed for, are apt to give conflicting results. When the lamp is first started the 2536 line is very intense, this condition remaining for about 30 seconds. The intensity then falls off to about one-third of its initial value, remaining low for two or three minutes, after which it gradually increases to the original value. This results from the self-reversal of the components of the line. At the start, the tube is cold and the mercury vapour liberated from the cathode surface condenses in fine drops on the wall : this keeps the pressure down and gives the high initial intensity of the line. The anode and tube gradually heat and this mercury re-evaporates causing reversal by absorption, in spite of the magnetic field, and a consequent decrease in the intensity. When the tube above the water surface is clear of condensed mercury, the reversal disappears, and we have a steady condition, the vapour evolved from the cathode condensing on the inner wall below the surface of the water.

2. A horizontal lamp, made of pyrex glass, with a quartz tube inserted as shown in fig. 2, was employed at one stage of the investigation. Connexion with the mercury vapour pump was effected by means of a piece of thick-walled rubber tube which had been soaked in castor-oil for several days. This lamp was started by tilting slightly and shaking. Its operation will be more fully described presently. Lamps

Even with the water-cooling some mercury condensed in the tube leading to the pump, and drops occasionally fell down and choked the capillary. It was found necessary to employ a stopcock between the tube and pump to prevent the vacuum from getting too high at the start. When the tube is well heated by the discharge the cock can be left open.

The Fine Structure of 2536.

The study of the line structure was commenced with the first type of lamp described, using the two Lummer-Gehrke plates crossed and a small quartz spectrograph. It at once appeared that the complicated structure found by Nagaoka resulted, in all probability, from absorption by mercury vapour in the neck of his lamp.

Fig. 1, Plate XXIV., shows the true fine structure of the 2536 line when the arc is operated on the minimum current (1·5 amperes) with the discharge pressed against the wall facing the interferometer by a magnetic field. There are five components of very nearly equal intensity, which I have numbered on one of the rows of interference dots. The separations of the components are ·014, ·010, ·011, and ·011 respectively. If we place a quartz bulb 2 cm. in diameter, highly exhausted and containing a drop of mercury, between the lamp and the interference plate, each dot becomes double by reversal, and we have a row of ten dots as shown by fig. 2. This shows us that all five components of the line are absorbed to about the same extent by mercury vapour at room temperature. As a matter of fact the stage shown in fig. 2 represents the absorption when the mercury vapour has a density corresponding to 0°, the stem of the bulb which contained the mercury drop being immersed in ice in this case. With the bulb at room temperature we get the condition shown in fig. 3. This required a longer exposure, as the dots are more heavily reversed, and we utilize only the fainter light at the edges of the dots. In this stage some of the adjacent dots have fused. If we number the dots in the reversed spectrum 1 to 10, we find that 4 and 5. 6 and 7, and 8 and 9 have fused, 1, 2, and 10 remaining isolated. This gives us an apparent structure of seven elements, while the structure found by Nagaoka, although resembling this in a general way, had six elements, one of them consisting of two, or possibly three fused dots, the structure being similar to that of fig. 6. A small insert in fig. 4, taken from Nagaoka's paper, shows the structure which he found.

As it seemed highly probable that the structure found by

Nagaoka resulted from absorption in the long column of unexcited vapour in the type of lamp which he used (Lummer-Arons), I made a lamp of this type modified in such a way that the length of the absorbing column of vapour could be varied or reduced to zero. The construction of the lamp is shown in fig. 2. It was made of pyrex glass, with the exception of the insert tube, which was of quartz, blown out to a very thin clear bulb on the inside. This tube could be pushed in until the thin bulb was immersed in the discharge, or withdrawn to any desired distance, and sealed with wax. The electrode bulbs and body of the lamp were wrapped with wet cotton, on which a stream of water ran continuously during the operation of the lamp. With this lamp the five-dot structure was obtained when the quartz tube was pushed all the way in, and the Nagaoka structure when it was withdrawn so that the light from the arc was obliged to traverse a column of unexcited vapour before it emerged from the tube. The fact that I was unable to duplicate the Nagaoka structure exactly by passing the light from the Cooper-Hewitt arc through mercury vapour of any density (the structure of seven components gradually fading away as the density of the absorbing vapour increased) caused me to think that there was something peculiar about the vapour in the neck of the Lummer-Arons lamp, and I wasted several weeks in experimenting with the lamp under different conditions of excitation, and with the quartz insert tube in various positions. The trouble was finally located, however. It seems that the double component of the Nagaoka structure is formed by the fusion of dots 2 and 3 of the reversed spectrum. This requires that the dots must be rather wide in the first place, or what amounts to the same thing that there must be some light even in the region midway between the dots. I found that if the Cooper-Hewitt lamp was placed in a stronger magnetic field the dots were widened by the Zeeman effect until they fused into an almost continuous band, as is shown in fig. 5, Plate XXIV.*
If the light from the lamp was then passed through the bulb containing mercury vapour at a sufficient density, the Nagaoka structure was at once obtained. The photograph reproduced in fig. 6 was obtained in this way. On this photograph I have numbered the dots 1, 2, 3, 4, 5, and 6, number 2 formed by the fusion of 2 and 3 of fig. 2.

The true, or five-dot structure in coincidence with the

* This print was inadvertently transposed during the process of en-largement and rotated through 90° in mounting. It can be correctly seen in a mirror if rotated 90°.

Nagaoka structure is shown by fig. 4 (Pl. XXIV.).   This photograph was made by making one exposure with the quartz tube of the Lummer-Arons lamp pushed in, the other with it pulled out, the plate-holder of the spectrograph being raised a small fraction of a millimetre between the two exposures. I have inserted the numbers 1 to 6 below the dots of the Nagaoka structure, the true structure of five dots being just above it.

The transition from the true, or five component structure to the more complicated types, which result from absorption, is shown diagrammatically in fig. 4.   Number 1. The five components, when the lamp is first started (with magnetic field on).   2. Components widened, in absence of field or with lamp at higher temperature.   3. Each component doubled by absorption, either by an auxiliary absorbing cell, or by operating the lamp at higher temperature.

Fig. 4.
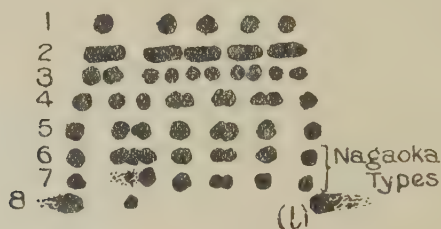
4, 5. Components of the dots fusing by increased absorption and broadening of the dots.   6, 7. Structure found by Nagaoka, also observed in the case of the "end-on" lamp. There appears to be no way of accounting for the middle component of the triple dot by absorption.   Of this more will be said presently.

8. This structure was found by Nagaoka when his lamp was operated by a current of 9·8 amperes.   In reference to it he says:—

"The loss of definition of interference points at the cathode is obviously due to bombardment by positively charged atoms while the anode is mostly penetrated by electrons.   With increasing current the molecular agitation plays an important part in affecting the source of light and brings about the result as shown in the photograms.   Why the end point (e) is only enhanced seems rather difficult to explain. It rather suggests that the line is excited in the electronic orbits according to the Bohr scheme, and not by the vibrations of the nucleus.   The increase in the intensity of the feeble

lines indicates the presence of violent atomic motions and
consequently the increase in nuclear vibrations, as is attested
by the black streaks in the photographs."

This seems to me to be extremely vague speculation, and
I am unable to follow his argument.

The structure is clearly the result of increased absorption,
combined with a broadening of the components. The widening
of the absorption lines obliterates all of the light between com-
ponents 2, 3, 4, and 5 as well as the components themselves:
a trace of light between 1 and 2 remains, owing to the greater
separation of these components ; this gives the faint dot.
The outer edges of 1 and 5 remain strong and are bordered
by " wings " as is to be expected. These wings, which are
identical with the wings which accompany all spectrum lines
when produced by heavy currents in dense vapour, are the
" black streaks " referred to by Nagaoka.

The explanation of why the Lummer-Arons lamp gave the
Nagaoka structure while the Cooper-Hewitt yielded it only
when placed in a magnetic field much stronger than that
used for deflecting the arc, is undoubtedly that the dots are
broader, *i. e.* have faint wings when the arc is viewed
" end-on," as was the case with the former lamp. Sub-
sequently I obtained a structure practically identical with
the Nagaoka structure with the Cooper-Hewitt lamp by
operating it with a current of 2 amperes without water-
cooling. In this case the structure is developed by the absorp-
tion of the layer of mercury vapour which surrounds the arc.

Nagaoka states that he obtained his structure with sharply
defined components only when the arc was immersed in ice
and exhausted continuously by charcoal in liquid air. My
first experiments were made with a lamp exhausted by a
powerful mercury-vapour pump in continuous operation, but
the results did not differ from those obtained with a com-
mercial Cooper-Hewitt lamp. It is probable that in the case
of Nagaoka's lamp the density of the vapour in the arc was
much greater than the density corresponding to zero degrees,
on account of local heating of the surface of the mercury
electrodes by the stronger current employed (2 to 4 amperes).
The lamp employed in the present work was operated at
1 to 1·5 amperes, with one electrode of mercury and the other
of tungsten. I am unable to explain the triple nature of the
group shown in Nagaoka's photographs, if it really exists.
In my photographs this group was always double, in cases
where the absorption resulted from an auxiliary cell con-
taining mercury vapour, used in conjunction with the water-
cooled lamp with the discharge magnetically deflected. In

the case, however, of the lamp with the quartz insert the structure appeared to be triple in some cases, as in Nagaoka's photographs, the relative intensities of the three components varying with the residue pressure in the lamp as shown by the McLeod gauge.   One of Nagaoka's photographs shows the three dots with very different intensities, as in the lower row of fig. 2, but the conditions under which it was taken are not given in his paper.

An attempt to photograph the fine structure of 2536 in the luminosity projected into a lateral tube from the arc was not very successful, owing to scattered light from the wall.   In view of results recently described by Lord Rayleigh on the spectrum of this luminosity, it is my intention to repeat the experiment under improved conditions.   The difficulty in explaining the three-fold dot may be cleared up in this way.

Effects of Nitrogen on the Absorption.

The remarkable effects of nitrogen at a pressure of a few millimetres on the absorption of the vapour already excited by the 2536 radiation, for the line of wave-length 4046, which I mentioned in the paper on the controlled orbital transfers, made it seem desirable to examine the effect of the gas on the absorption of the components of the 2536 line. It was found that the only effect was to increase the magnitude of the absorption in a very marked degree.   The magnitude of the effect of nitrogen at 3 cm. pressure is about the same as that obtained by raising the density of the mercury vapour from its value at zero degrees to the value which obtains at 20°, which is roughly a tenfold increase.

Zeeman Effect.

The study of the effect of a magnetic field on the components of the 2536 line was more difficult than had been expected.   The quartz mercury arc is extinguished instantly in fields of only very moderate intensity, and the high potential discharge of a transformer in a quartz capillary was somewhat erratic in its behaviour, required long exposures, and caused a rapid deterioration of the tube.

In only one case could the interference dots be split into distinct components, consequently no attempt was made to secure quantitative data. A Ruhmkorff magnet was employed the flat pole-pieces of which were separated by a distance of about 3 cm.   Employing the high-potential discharge-tube, it was found that with 3 amperes flowing in the magnet the

fringes of the 4046 line formed by the larger of the two interference plates were split into two components, of separation such as to give a system of equally spaced fringes of twice the number and half the separation as obtained without the magnetic field.

With the quartz mercury arc between the pole-pieces of the magnet and a current of only 0·4 of an ampere the interference dots were widened by a very slight amount, while with 0·8 of an ampere dots 2, 3, 4, and 5 of fig. 1 were spread out into an unbroken line while dot 1 was considerably widened.

In some cases, with 1·35 amperes flowing in the magnet component number one was distinctly divided, while 2, 3, 4, and 5 remained fairly sharp and single. With 3 amperes they were still visible as separate dots. These results are not very consistent, and it is quite impossible to come to any very definite conclusion. Some form of discharge-tube more constant in its behaviour will have to be designed, and the interference plates will have to be adjusted to give the sharpest possible definition. The alternating high-potential discharge is deflected against opposite walls of the capillary by the magnetic field which complicates matters, as we have two sources of radiation, one accompanied by absorption, the other free from it.

Some observations were also made on the effect of the magnetic field on the absorption of mercury vapour. An exhausted bulb of quartz containing a drop of mercury, and furnished with a long stem for temperature control, was placed between the pole-pieces and the light of the arc transmitted through it. With the stem in a bath at 8° and zero field the five dots were all doubled as in fig. 2, Plate XXIV. With 0·5 ampere in the magnet, components 2, 3, 4, and 5 were fused to a continuous line, and component 1 much widened. With 1·25 amperes the five dots appeared sharp and single as in fig. 1, Plate XXIV., in other words all traces of absorption had disappeared; the absorption lines had evidently doubled allowing the light of all five components to pass between them. With 3 amperes the appearance was practically the same, but with 4 amperes dots 1 and 5 were strong, while 2, 3, and 4 were very faint. At 4·8 amperes 1 and 5 were strong, 3 fairly strong, and 2 and 4 faint. These results clearly cannot be explained by the summation of the absorptions of widening doublets ; for if the magnetic components crossed as the separation increased, the left-hand component of 5 and the right-hand component of 3 would coincide with emission component 4 and obliterate it, while

5 would be absorbed only by the right-hand component of 4, *i. e.* the absorption of 6 would be only one-half as great as the absorption of 4. Applying this to the other components, we should expect 1 to be very strong, 2 and 5 less strong, and 3 and 4 very faint, which is contrary to observation. There is evidently a mutual influence between the components, the effects being analogous to those observed by Paschen and Back in the case of close doublets and triplets.

This subject will be further investigated during the coming autumn.

I have been greatly aided in this investigation by a grant from the Rumford Fund of the American Academy of Arts and Sciences.

LXXXII. *Optical Excitation of the Mercury Spectrum, with Controlled Orbital Transfers of Electrons. By* R. W. Wood, *For. Memb. R.S., Professor of Experimental Physics, Johns Hopkins University* *.

[Plate XXV.]

IN the Proc. Roy. Soc. cvi. p. 679 (1924) I gave a preliminary account of experiments made with a view to confirming experimentally Bohr's theory of the absorption and emission of light by the vapour of a metal in both the normal and excited state. Briefly stated, this theory assumes that the vapour, in the normal state, can absorb only radiations of wave-length corresponding to lines emitted when electrons from higher levels (orbits) fall to the orbit in which the electron revolves in the normal state. In the case of mercury there are but two such lines of which the absorption has been observed, the 1849 and 2536 lines corresponding to transfers from the 2P and $2p_2$ orbits to the 1S orbit, the orbit of the electron for the vapour as it exists normally in the unexcited state. The theory further supposes that the electron raised, say from the 1S to the $2p_2$ orbit by the absorption of the 2536 radiation, may either return to the 1S orbit with the emission of 2536, or may be carried to outer orbits by the absorption of other radiations corresponding to the fall of electrons from these orbits to the $2p_2$ orbit. A mercury atom with the electron raised to the $2p_2$ orbit by the absorption of the 2536 radiation of a mercury arc is in the excited state, and may now absorb any one of the

* Communicated by the Author.
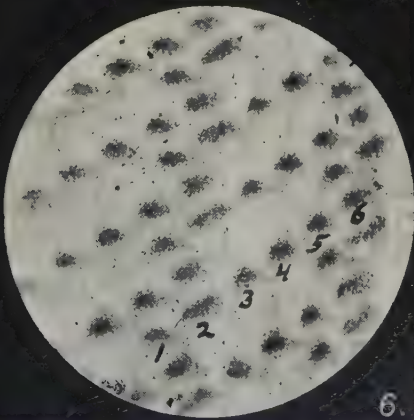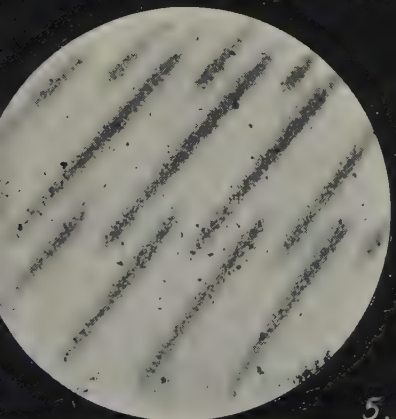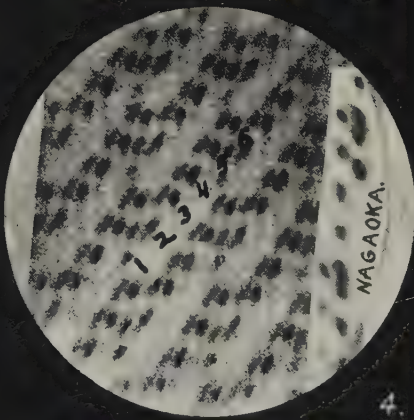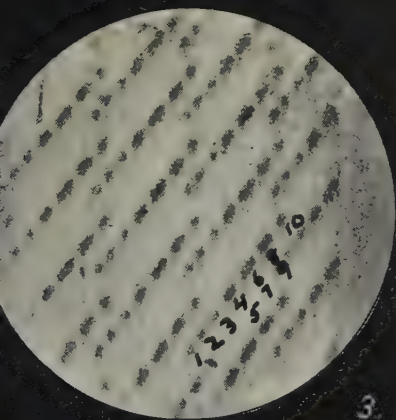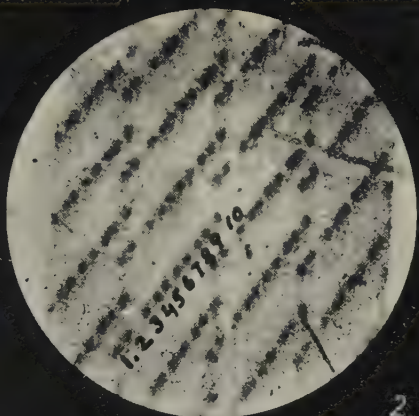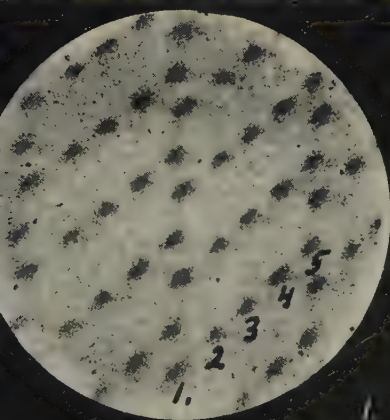
following radiations and be raised thereby to the orbit designated: 4358 (2s), 4077 (2S), 3125 (d'), 3131·5 (d''). 3131·8 (3D), 2894 (3s), 2655 (4D), 2652·4 (2d'), and 2653·7 (2d''), and others corresponding to lines of wavelength shorter than 2536 which are not considered in the present work, as the lines corresponding to them are very faint. From these outer orbits they may fall back not only to 2p_2 from which they were raised, but to any other of the inner orbits allowed by the selection principle, consequently the vapour may emit practically the complete arc spectrum.

Fig. 1.
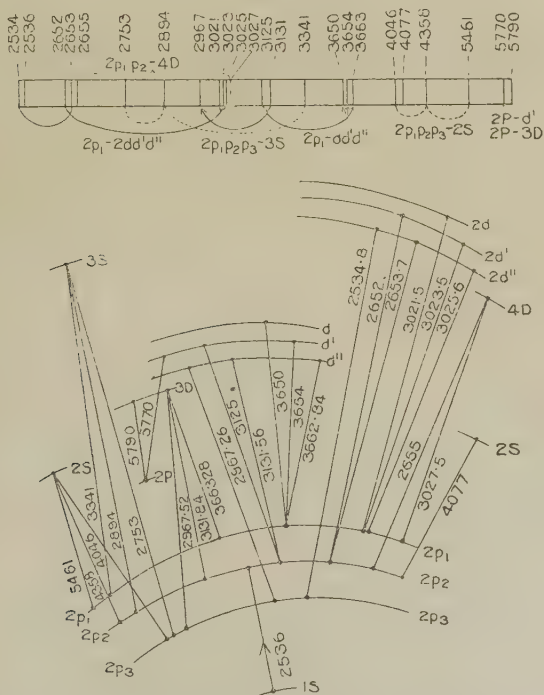
The orbital transfers involved in the present discussion are shown in fig. 1, with the corresponding lines of the mercury spectrum just above. This is essentially a Grotrian diagram with the energy levels separated into groups. I have found it a little easier to follow out the transitions on a diagram of this type than on the one commonly employed. No attempt has been made to space properly the different levels, since, if this were done, the d levels would be so close together as to be useless for the purposes of the diagram.

Referring now to fig. 1, we will follow out, as an illustration of what is to be expected on the Bohr theory, a single possible case of successive absorptions and emissions which may occur when mercury vapour at room temperature in a quartz tube highly exhausted is illuminated by the light of a quartz-mercury arc.

By the absorption of the radiations of wave-length 2536 the electron in an atom is raised from 1S to $2p_2$, on which orbit it is in a condition to absorb any one of the radiations previously enumerated. Suppose that it absorbs the radiation 3125 and is carried up to d'. From here it can either fall back to $2p_2$ with emission of 3125, or to 2P with emission of the yellow line 5770, or to $2p_1$ with the emission of 3654.

If we could restrict our illumination to the two wave-lengths 2536 and 3125 we should expect an emission spectrum consisting of one yellow, one violet, and the ultra-violet line, in addition to the resonance radiation 2536, caused by the fall of electrons from $2p_2$ back to 1S, before they had time to exercise absorption. In the same way the absorption of 3131·56 by raising the electron to d'' can cause the emission of 3662·84 and 2967·26, but 3650, the other member of the close group of three lines, cannot appear as a *direct* result of any absorption occurring at the $2p_2$ level, as none of these carry an electron to the d level. This line can appear only by the absorption of 3650 by atoms with electrons on the $2p_1$ level, to which they may be brought by the emission of 3654 and 3662·84, as just described ; they may also be brought to this level by the absorption of 4358, which carries them to the 2s level, from which they may fall to $2p_1$ with the emission of the green line. In the course of the present paper it will be shown that the emission of 3650 is much stronger when excited in the latter manner.

A large percentage of the electrons raised to $2p_2$ return at once to 1S, giving rise to resonance radiation, which I have described in various papers, and that a process of the second type considered also took place was shown by Fuchtbauer, who found that, under very powerful illumination, a large number of lines of the mercury spectrum were radiated in addition to the 2536 resonance radiation. He showed that, if the 2536 radiation was screened off by glass, none of the other lines appeared ; but he did not show that excitation by lines other than 2536 was necessary for the emission of the complete arc spectrum. This must, of course, be true on Bohr's theory, but a less modern explanation might be that the absorption of the 2536 radiation created some sort of disturbance in the atom which caused it to emit its other frequencies

as fluorescence. At all events it appeared to be worth while to show by actual experiment that the successive absorptions and emissions took place in the manner imagined by Bohr. To do this we must illuminate the vapour simultaneously with two or more monochromatic mercury radiations, one of them being 2536, and study the resultant emission. It was found that this could be accomplished by mounting one or more water-cooled quartz-mercury arcs (of the vertical type with tungsten anode) close to the vertical quartz tube containing the mercury vapour at room temperature *in vacuo*. Between these lamps and the "resonance tube," as we may call it, various ray filters were introduced, for the purpose of restricting the range of the exciting radiations. As the walls of the resonance tube are very powerfully illuminated and scatter much light, it was impossible to employ a bulb at the upper end, for it is impossible to blow a bulb of quartz which will not deflect much of this light to the spectroscope, and give a strong arc spectrum of mercury superposed on whatever we are getting by optical excitation. The right-angle prism, attached to the open end on the resonance tube with Boltwood's wax (of low vapour-tension), must be flawless and free from scratches. A single scratch on its surface will produce a spectrum quite as bright as the spectrum that we are studying. For the same reason, its surfaces must be super-clean, the slightest smear of dirt or grease being fatal. It is best to clean it with the same care that is employed in cleaning glass for silvering, polishing it with clean absorbent cotton that has never been handled. It should be examined at every angle in a very strong light (preferably sunlight) against a black background, and if the slightest smear can be seen, it should be polished again. If these precautions are not taken, it is useless to hope to get the fainter of the optically-excited lines uncontaminated with scattered light. As this method of studying spectra appears to be novel, and of considerable promise, I shall give a brief *résumé* of certain portions of the earlier paper.

The arrangement of the apparatus is shown by fig. 2. The quartz arc is immersed, as shown, in a glass tube filled with water, which runs in at the bottom and overflows at the top, the stream being carried to a sink by a tin gutter. The resonance tube of quartz is drawn off at the bottom as shown, and painted black on the outside, the arrangement which I adopted for securing a black background in the experiments on the resonance radiation of iodine vapour. A right-angle prism of quartz is cemented to the top of the tube, and the quartz spectrograph mounted with its slit at a distance of

about 30 cm. from the prism. A diaphragm placed close to the prism limits the light reaching the slit to that emitted by the vapour in the tube. The slit of the spectroscope must be reduced to a length of about 1 mm., and the hole in the diaphragm made of such a size as just to cut off the light diffused by the walls of the tube. These adjustments are made by bringing the eye up to the focussed spectrum without an eyepiece. It is not sufficient to restrict the

Fig. 2.
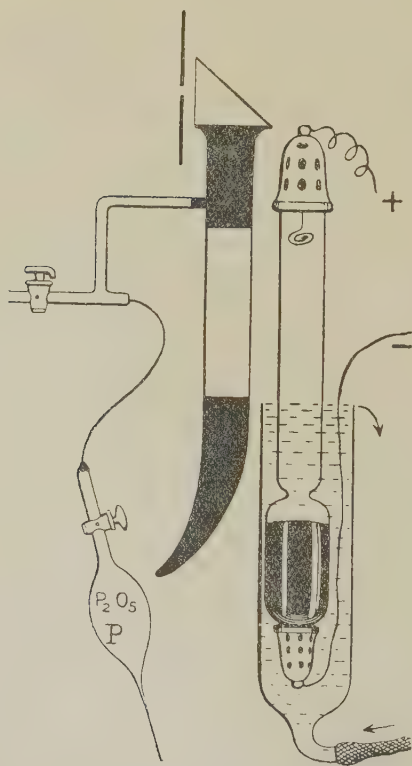
field by the iris diaphragm in the spectrograph, since narrowing the slit will cause it to gather light from the walls of the tube, though they may have been quite invisible when viewed through the spectrograph with the slit at moderate width. The diaphragm must be at the prism face, as shown.

Both the water-cell and lamp were mounted on the same tripod laboratory iron stand, the arc being clamped by its

upper terminal (see fig. 1 in previous paper). This method of mounting is much more convenient than the one formerly used, as the lamp can be started by merely tipping the iron stand on two of its feet until the arc strikes. The method insures a constant depth of immersion and fixed position of the lamp.

The resonance tube was much larger than the one employed before ; its length was 35 cm. and its diameter 3 cm. It was longer than is indicated by the figure, to avoid heating the prism by the hot-lamp terminal. It contained a drop of mercury, and was exhausted by a mercury vapour pump with a McLeod gauge in the circuit. Nitrogen was admitted from the bulb, containing phosphorus and phosphorus pentoxide, through a long fine capillary tube.

The resonance tube was, in certain cases, illuminated by a second quartz arc, not water-cooled. By the use of both arcs simultaneously a wider range of monochromatic combinations can be employed for the excitation. For example, a bromine filter may be placed between the water-cooled arc and the resonance tube, the filter consisting of a large cell of fused quartz, 2 cm. thick, filled with bromine vapour at room-temperature tension. This transmits 2536, 2967, and 3125–3131. No visible radiations except the yellow lines are excited by this stimulation, though the spectograph shows the presence of the lines 3654 and 3663 of the ultra-violet triplet. The second arc is now lighted. The light of this arc alone produces no radiation of the mercury vapour, since, not being water-cooled, its 2536 line is reversed, and incapable of bringing the atom into the excited condition. But the vapour has been excited by the 2536 radiation of the water-cooled arc, and in this condition is able to absorb the violet line 4358 of the second arc, the electrons passing out to the $2s$ orbit, Falling back from here to $2p_1$ they emit the green line 5461, as was proved by putting a sheet of dense cobalt glass between the resonance and the high-temperature lamp. The green radiation persisted, though only the violet light of lamp entered the tube.

The study of the fine structure and absorption of the 2536 mercury line, reported in the previous paper, showed the importance of applying a transverse magnetic field to the exciting arc. Under ordinary circumstances, even with the water-cooled arc, the five components of the line are strongly reversed, but with the magnetic field on, the discharge is pressed against the wall of the tube and the reversal avoided.

In the course of the present work a number of unexpected

facts have come out, which have thrown much light on some
of the discrepancies and inexplicable phenomena found in
the earlier investigation. In the first place, it was found
that the relative intensities of the arc lines changed in a
surprising manner during the first two or three minutes of
the arc's operation. It was noticed that a droplet of mercury
sometimes stuck to the wall of the tube near the anode.
This evaporates under the radiant heat of the electrode, and
the intensity ratios between the various lines are very
different before and after the final disappearance of the drop.
This circumstance was not detected until the investigation
was well under way, so that many of the earlier plates cannot
be discussed with certainty. It was found that during the
first few minutes of operation the lines 4077, 3654, 3663
decreased considerably in intensity, while 3125 and 3131
increased slightly, and 3650 very much. It was found also
that the application of a magnetic field to the exciting lamp
not only increased the intensity of the optically-excited
spectrum, but that some of the lines were enhanced with
respect to the others, 3650 in particular. As we shall see
presently, this is a line of especial interest.

The observation recorded in the earlier paper that filtering
the exciting light through a thick block of crystalline quartz
caused the suppression of this line, has been found to be
incorrect, at least that is my opinion at the present time.

There is, too, some question in my mind about the dif-
ference between the intensity ratios of the lines 2967, 3131,
and 3663 in the case of excitation with and without the
bromine filter, reported in the earlier communication, as I
have not confirmed it in the present work. The discrepancy
may, however, be due to the circumstance that, in the earlier
work, no magnetic field was applied to the lamp. Next year
I plan a very careful photometric determination of intensity
ratios under all possible conditions of excitation. The
present work has been largely qualitative, with a view of
finding out what could be done with various filter com-
binations, and what the various factors were which altered
the intensity ratios of the lines.

Under the continued operation of the lamp, the inner wall
of the resonance tube becomes discoloured by a brown film,
as I reported previously. I now believe that this may be
carbon deposited as a result of the presence of vapour from
sealing-wax or stop-cock grease, and not from a reduction of
the silica by the excited mercury atoms, as I once thought.
It has given much less trouble this year, since I have used
Boltwood wax instead of sealing-wax and a powerful mercury-

vapour pump in place of the Gaede rotary pump used last year, which was not very clean.

If the resonance tube is cut off from the pump the pressure goes up rapidly, as shown by the McLeod gauge, as a result of the liberation of some vapour (probably water) by the action of the excited mercury atoms, and in some cases the spectrum of the so-called ultra-violet "water-band" appears just below the 3125 line. This is shown on Pl. XXV. (fig. 5 *b*), together with some other bands (probably due to nitrogen which was in the tube) between the 3341 and 3650 mercury lines. On another plate (fig. 5 *c*) a group of bands appeared between 3341 and 4358 : in this case the resonance tube contains navy helium, which had been in contact with charcoal at room temperature. I was inclined to ascribe them to CO or CO_2, but have been unable to reproduce them with gas mixtures prepared in other ways. The water-band alluded to above is developed by the presence of nitrogen in the tube, but if we introduce water-vapour into the vacuum, it causes only the continuous band below 2967, as shown by fig. 5 *d*.

These bands are excited by the excited mercury atoms in a manner analogous to the excitation of thallium and lead lines by optically-excited mercury vapour described by Franck and Cario.

Before taking up the more recent results, obtained with various filter combinations, it will be necessary to consider the mercury arc spectrum as a whole, paying some attention to the relative intensities of the lines, in its relation to the optically-excited spectrum, for the relative intensities of related lines give us information regarding the manner in which a number of electrons, all on the same high level, distribute themselves among the possible lower levels to which they fall. An important question to be solved is whether the distribution among the lower levels is independent of the manner in which the electron has been brought to the high level; for example, is the intensity ratio of the lines 2967·26, 3131·56, and 3662·84, which all originate on the d'' level, the same in the arc and in optically-excited vapour ; and is it immaterial whether the electrons are raised to d'' by absorption of 2967·26 from $2p_3$ or by 3131·56 from $2p_2$?

In the mercury spectrum, as represented in the diagram (fig. 1) and in the following table, the lines 3663, 3131, and 2967 are in reality double, as they are given by electron falls from 3D and from d'' to $2p_1 p_2 p_3$, as is clear from the diagram. The spectroscope used in the present investigation does not separate them, however.

We have similar pairs of lines from the 4D and 2d levels. In this case 2653 and 2655 are clearly separated by the spectroscope.

The relative intensities of the lines in the mercury arc spectrum are given in the following table :—

λ.		Intensity.		λ.	Intensity.
				5790	100 (rough
$2p_1p_2p_3$–2s ...	$\begin{cases} 5461 \\ 4358 \\ 4046 \end{cases}$	400 (estimated). 200 100.		5770	100 estimate).
			$2p_2$–4S	4077	30
$2p_1p_2p_3$–3s ...	$\begin{cases} 3341 \\ 2894 \\ 2753 \end{cases}$	8 4 2	$2p_1$–4D	3027 (faint, not measured).	
			$2p_2$–4D	2655	
$2p_{,}$–$dd'd''$	$\begin{cases} 3663* \\ 3654 \\ 3650 \end{cases}$	30 30 60	1S–$2p_2$	2536	400
$2p_2$–$d'd''$...	$\begin{cases} 3131* \\ 3125 \end{cases}$	50 30	$2p_1$–3D $2p_1$–d''	3663·28 3662·88	20 10
$2p_3$–d'' ...	$\begin{cases} 2967* \end{cases}$	12	$2p_2$–3D $2p_2$–d''	3131·84 3131·56	20 30
$2p_1$–2$dd'd''$	$\begin{cases} 3025 \\ 3023 \\ 3021 \end{cases}$	0·3 2 8	$2p_3$–3D $2p_3$–d''	2967·52 2967·26	10 2
$2p_2$–2$d'd''$	$\begin{cases} 2653 \\ 2652 \end{cases}$	2 4			
$2p_3$–2d'' ...	$\begin{cases} 2534 \text{ (not measured).} \end{cases}$				

* Includes the intensities of lines originating from the 3D level.

These intensities were determined by matching different lines of spectra taken with exposures of 5, 10, 15, 20, etc. seconds ; the plates being held in contact film to film, and the lines to be compared brought into contact with each other. More accurate determinations will be made in the autumn with the arc operated under the varying conditions in which it has been employed in the present work.

The lines have been arranged in the order in which they appear in the various series of the mercury spectrum. The intensities of the unresolved double lines 3663, 3131, and 2967 are given in the table, as these are the values to be compared with that of the corresponding lines of the optically-excited spectrum. At the end of the table I have given the intensity values which the components of the double lines would have on the same scale as that of the other lines.

These values were calculated from photographs made with a grating of 2-metres focus in the third-order spectrum, correcting the values from the supplementary table (*i.e.*, eliminating the 3D part of the intensity).

We see that the intensities of the lines $2p_1-dd'd''$ are in the ratio $6:3:1$ *, while the lines $2p_1-2dd'd''$ are in the ratio $24:6:1$. I do not feel very certain about the last values, as they were not well separated by the spectrograph. Fowler gives the ratio as $5:4:2$. I am sure, however, that this is incorrect. The ratio for $2p_2-dd''$ is $1:1$, while that for $2p_2-2dd''$ is $2:1$.

The intensity ratios of the lines in the optically-excited spectrum may be varied in an almost unlimited degree by modifying the conditions of the excitation. As an illustration, we may take the group 3650–3654–3663, which in the arc have the ratio $2:1:1$ when photographed with small dispersion not resolving 3663.

On Pl. XXV. (fig. 1) we see this group under various conditions : (*a*) with 3663 slightly more intense than the other two, taken with mercury in air at 0·1 mm. ; (*b*) with 3650 practically absent, taken with bromine-filtered excitation.

Change in the Intensity Ratios of the Optically-excited Lines as a Result of applying a Magnetic Field to the Exciting Lamp.

As I have shown in the previous paper, the radiations of the 2536 mercury line can escape from the lamp unmodified by absorption, only when a magnetic field is applied to the arc driving the discharge against the wall, and squeezing out, so to speak, the thin layer of non-luminous vapour which normally surrounds the arc. Taking this precaution, the line was found to consist of five components of nearly equal intensity, the total width of the group being only 0·05 Ång. In the absence of the field, each line is divided into two by reversal, and we have a group of ten lines. It is clear that, under these conditions, the excitation of the vapour in the resonance tube will be less powerful, since the effective " core " of each one of the components has been removed by absorption. With the magnetic field on the arc we increase (perhaps 8-fold) the number of electrons raised from 1S to $2p_2$, and the optically-excited lines increase in brilliancy as a result. Most remarkable, however, is the fact that the increment of the 3650 line is *twice* as great as that of the other lines, while the increment of 2536 (resonance

* On plates made with the grating, the ratio was $5:3:1$.

radiation) is only *half* as great. The photometric measurements were made by taking a series of exposures of 2, 3, 4, and 5 minutes' duration with the field, and one of 24 minutes without the field.

The increments due to the field were as follows :—

Line 2536, four-fold ; lines 5461, 4358, 4046, 3663, 3654, 3131, 3125, 2967, eight-fold ; line 3650, sixteen-fold.

Omitting, for the moment, the unique increment of 3650, we can make an interesting hypothesis to account for the 4-fold increment of the 2536 resonance radiation, and the 8-fold increment of the other lines. With the magnetic field on, we have the components of 2536 unmodified by absorption in the exciting lamp, and consequently of greater intensity than without the field ; hence more electrons will be carried from 1S to $2p_2$.

This seems self-evident. We will now make the hypothesis that in this case, where there is "sharp tuning" in the excitation, the electrons are carried exactly to the $2p_2$ level, at which level a certain proportion are carried up to higher levels by absorption, and give rise to the other lines on their return : the remainder return to 1S with emission of 2536 resonance radiation. The proportion carried to higher levels, with the magnetic field "on" is evidently greater than with the field "off," as is shown by the 8-fold increment of the other lines and the 4-fold increment of 2536. This means that when the electrons are carried to $2p_2$ by the absorption of the "reversed" components of 2536, a smaller proportion is carried up to higher levels, *i. e.* they are more likely to fall back to 1S. We may perhaps ascribe this, as I have hinted above, to the circumstance that, with "inexact tuning," they are not raised exactly to the $2p_2$ level, and hence are less likely to exercise absorption for lines which terminate on this level. Very little attention was paid to the intensity of 2536 in comparison to that of the other lines during the investigation, as it was not realized that it had any significance, the above-mentioned change of ratio not being noticed until the plates were more carefully examined after the close of the experimental work. Better and more complete photometric measurements will be made in the autumn.

The greater enhancement of the 3650 line is probably due to the circumstance that this line is enhanced in the spectrum of the mercury arc by the application of a magnetic field, as was pointed out earlier in the paper. It will be recalled that the 3650 line appears only as a

result of the absorption of light of this wave-length, at least when the mercury vapour is in a high vacuum.

If the resonance tube is shut off from the pump, and the pressure allowed to rise to, say, 0·03 mm. from gas liberated from the tube walls by the optically-excited vapour, the enhancement of 3650 is not greater than that of the other lines. I believe that this is associated in some way with the circumstance that the 3650 line can be strongly developed by the presence of small traces of other gases in the tube, even with the absence of the 3650 radiation in the exciting light, as has already been pointed out.

With nitrogen at 3 mm. in the resonance tube, applying the magnetic field to the lamp increases the intensity of all of the lines about 3-fold instead of 8-fold, as is the case when the vapour is in a high vacuum. This seems to indicate that "sharp-tuning" plays a less conspicuous rôle in the presence of a foreign gas.

Excitation by Bromine Filtered Light.

If a filter of bromine vapour contained in a cell of fused quartz is interposed between the mercury arc and the resonance tube, the wave-lengths 4036 and 4358 are removed from the exciting beam, and very interesting changes occur in the optically-excited spectrum.

The dimensions of the filter were $14 \times 4 \times 1$ cm. (internal), a flat cell being preferable to the cylindrical one used in the earlier work, since it permits of a closer approach of the lamp to the resonance tube. The cell was constructed without much difficulty from two flat plates of very clear fused quartz made by the General Electric Co., and four thick quartz rods, 7 mm. in diameter, clamped together to form a cell, and fused along the edges in a powerful oxy-hydrogen flame. One of the quartz rods was cut a little shorter than the other, leaving a small hole at one corner of the cell, which was closed by a short length of quartz tubing fused to its edge. The sides of the cell, having become frosted in spots by devitrification, were now heated to the softening-point in the flame and blown out a little, increasing the thickness of the cell to a little over 1 cm. About six drops of bromine were placed on the floor of the cell, through a small thistle tube; the cell was then warmed, causing the evaporation of the bromine and the expulsion of the air, and the tube fused in the flame. In using the cell it is very important that no fluid bromine is condensed on the walls. This can be prevented by warming the walls in a flame,

keeping the bottom of the cell cool. When in place between the lamp and the resonance tube, the heat of the lamp will keep the walls free from condensed liquid, especially if the water overflow cools the bottom of the cell.

Looking down the resonance tube through the prism, we see that the colour of the light now emitted is yellow instead of green, as is the case without the filter.

In the earlier work, in which the arc was used without the magnetic field, I was never able to see any luminosity in the resonance tube when using the bromine filter, which, however, was thicker than the one employed in the present case. The absorbing power of the present cell was determined by photographing the mercury arc through it, with exposure times of 100, 50, 25, 12, 6, and 3 seconds, and without the filter 1 second and 1/5 of a second. The 4046 line was reduced to about 1/500 of its normal value, the 4358 line to about 1/300. The 3650–3663 group was reduced to perhaps 1/3, and the lines of shorter wave-length down to about 1/2 normal value.

The orbital transfers involved are shown in fig. 1.

The electrons are raised from the 1S orbit, by the absorption of 2536, to the $2p_2$ orbit, from which a small proportion, perhaps 5 per cent., are carried up to d' and d'' by the absorption of 3125 and 3131. The remainder fall back to 1S, with the emission of 2536 resonance radiation. Of those lifted to d' and d'' some fall back to $2p_2$ with the emission of 3125 and 3131. The remainder drop to other levels. Of those on d', some go to $2p_1$ with emission of 3654, others to 2P, radiating the yellow line 5770 ; those on d'' divide themselves between the levels $2p_3$ (radiating 2967) and $2p_1$ (radiating 3662·8). No trace of the line 3650 appears in the spectrogram of the vapour, since no electrons are carried to d, though its appearance is theoretically possible, since the electrons on the metastable orbit $2p_1$ could be carried up to d by the absorption of 3650, which is present in the exciting light, though in reduced amount. With a prolonged exposure we do, in fact, get a trace of 3650 as a result of this process. It must be noted that the 3D level is also involved in the present case, in a manner exactly similar to that of d'', giving rise to the so-called inter-combination lines 2967·53, 3131·84, and 3663·28. The spectrograph used in the present work does not separate these lines from the lines 2967·26, 3131·56, and 3662·84, which originate from the d'' level.

Some of the electrons on 3D fall to 2P with the emission of the other yellow line 5790. There may also be a transfer

from d'' to 2P, which yields the very faint yellow line close to 5790 in the mercury arc spectrum.

The yellow lines might also originate from electrons raised from 1S to 2P by the absorption of 1849, and subsequent absorption of the yellow lines of the exciting lamp, but I found no evidence of such excitation. Metcalfe and Venkatesachar in their first paper * reported the yellow lines as not perceptibly absorbed by electrically-excited vapour, though in a second paper † they state that absorption of these lines was observed. Presumably the absorption co-efficient for the lines is small, which would account for their failure to appear from the process involving the 1849 line.

The appearance of the group 3650–3654–3663 when excited by the total radiation of the arc is shown on Pl. XXV. (fig. 1 a) when excited by the bromine-filtered radiation by fig. 1 b.

The emission of 3650 in the former case results from the electrons thrown down to the $2p_1$ level from $2s$ (with emission of 5461), to which they have been raised from $2p_2$ by the absorption of 4358, as shown in fig. 1. When on the $2p_1$ orbit, they are in condition to absorb 3650 from the exciting beam, in which it has a much greater intensity than either 3654 or 3663.

If we remove 3125 and 3131 from the exciting light, as was done in the earlier work with a filter of salicylic acid, the group 3650–3663 appears only as a result of electrons thrown down on $2p_1$ by the 5461 emission, where they absorb 3650–3654 and 3663. In this case 3650 is much stronger than the other two lines, since it is stronger in the exciting light. In this case three successive stages of absorption have occurred, namely 2536, 4358, and 3650–54–63. With 3125 and 3131 present in the exciting light, 3654 and 3663 in the emitted light appear as a result of a two-stage absorption only, viz. 2536 and 3125–3131, *i. e.* the emitted wave-lengths are not present in the exciting light. It is evident that the number of electrons passing to $2p_1$ from $2s$ is much greater than the number coming from d' and d'', as the green line is enormously brighter than the two violet lines.

I was for a time somewhat mystified as to why the electrons thrown upon $2p_1$ from $d'd''$ seemed to be practically inoperative in causing the appearance of 3650, while those passing to $2p_1$ from $2s$ were very efficient. There seems, however, to be no real difficulty. Electrons may be brought

* Proc. Roy. Soc. c. p. 149 (1921).
† Proc. Roy. Soc. cv. p. 520 (1924).

down to the $2p_1$ level from $2s$ without any emission of the group of three violet lines; those carried up to d by the absorption of 3650 must *all* return to $2p_1$, as no other transition is allowable, while those carried up to d' and d'' may in part fall back to $2p_2$ instead of to $2p_1$.   We should thus expect 3650 to be more intense than its neighbours, even if the intensities of the three lines were all equal in the exciting beam.   The case, as just considered, is for excitation with the salicylic acid filter, which removes 3125 and 3131.

For excitation without any contribution from $2s$, as with the bromine filter, the act of bringing the electrons to $2p_1$ from d' and d'' caused an emission of 3654–3663 ; and if only a small proportion of these, as is extremely probable, are involved in the third-stage absorption and re-emission (of 3650–54–63), the intensity of 3650 would be very small. With a much larger number coming to $2p_1$ from $2s$, the 3650 line would build up in intensity, even if only a small proportion of the electrons on the $2p_1$ were utilized in this way.

It is also possible to bring out the 3650 line without feeding electrons to the $2p_1$ level from $2s$, by the method of duplex excitation, employing a second quartz mercury arc operated on minimum current, but not water-cooled, and a filter of nickel-oxide glass, which transmits only the radiations 3650–54–63.   This more than compensates for the loss of intensity which these radiations have experienced in passing through the bromine filter, and the absorption and re-emission of 3650 is sufficient to give the line an intensity comparable to that of the other two lines.

It is apparent from the photograph taken with bromine-filtered excitation that 3654 is somewhat more intense than 3663.   This is important because, as I shall show presently, by the addition of air at a pressure of only ·03 mm. to the mercury vapour the intensity of the 3131 line can be greatly increased in comparison to that of 3125 : this means that more electrons are being sent to the d'' level, and consequently 3662·8 is enhanced, as is clear from fig. 1.   Accompanying this an increase in the intensity of 2967 is also observed, since this line results from the fall of electrons from d'' to $2p_3$.

Excitation by Chlorine Filtered Light.

The chlorine cell was made of very clear polished plates of fused quartz in the form of a box measuring $15 \times 4 \times 4$ cm., with quartz tubes inserted into the flat end-plates.   It was constructed for me in the Research Laboratory of the General

Electric Co., and has proved a most useful piece of apparatus, as it can be filled with aqueous or alcoholic solutions, and when used as a filter gives a 3-fold illumination owing to the total reflexions from the side walls, the effect being the same as if three arcs were used instead of one. This effect was first observed in the earlier work when the thick block of quartz was used as a filter, and I was at first unable to understand why the interposition of the block, which necessitated the removal of the arc to a greater distance from the tube, gave a more intense excitation.

The cell was filled with chlorine at atmospheric pressure, and was found to give the following absorption :—

Reduction of intensity of 4358 to 1/2, of 4046 to 1/4, all other lines down to 2753 to less than 1/2500, 2652 to 1/2, and 2536 to 1/3.

The excitation produced by light which has passed through this filter is thus restricted to 2536, 2652, 4046, and 4358, and we have in the emission spectrum only the three $2p–2s$ lines. This in itself is of no especial interest, the chlorine filter being of use chiefly for the purpose of duplex excitation in connexion with a second lamp.

It was also found that the introduction of nitrogen caused the appearance in the optically-excited spectrum of the lines which were not present in the exciting light. Of this, more will be said in the section dealing with the effects produced by gas admixtures.

By using the chlorine and bromine cells in combination, we can restrict the exciting light to the 2536 radiations, and then further excite with monochromatic radiations from either a second lamp or the same lamp by reflexion of the light through some such polarizing system as I have employed for the separation of the D lines of sodium for monochromatic illumination.

An enormous advance will be made as soon as the technique of this method is worked out. It seems hopeless to try to do anything with a prism monochromator ; but if the rotary polarization or double refraction of quartz is made use of I believe that it may be possible to illuminate the vapour with such combinations as 2536–3131, 2536, 3125, etc. The ideal method, of course, would be to devise some method of building up alternate layers of two substances transparent to ultra-violet light, of different refractive indices on a quartz plate, the system operating like a chlorate of potash crystal. Experiments along this line will be commenced shortly.

Effects of Nitrogen and other Admixtures.

In the earlier communication, I described the very remarkable effects produced by the introduction of nitrogen, helium, and other gases into the resonance tube. For the complete discussion of the more recent results it will be necessary to give a brief *resumé* of the phenomena as observed last year with an exciting lamp operated without a magnetic field. The admission of nitrogen, prepared from air by phosphorus, at a pressure of from 2 to 200 mm. to the resonance tube causes an immense increase in the intensity of the light, a green glow being visible through the walls of the tube, in spite of its proximity to the mercury arc. It appears to be associated with the presence of water vapour, as the so-called water band appears together with the mercury spectrum. This band is shown in Pl. XXV. (fig. 5 *b*) to the left of the 3125 line. With continued illumination of the tube the radiation becomes less intense, and the water band gradually disappears though the nitrogen pressure remains the same (fig. 5 *a*). After an illumination of two hours it has practically disappeared, and the green light is no longer visible through the side of the tube. I was unable to produce this enhancement of the light with nitrogen made from air which had been passed over hot copper, a circumstance probably due to presence of hydrogen in the nitrogen made in this way.

The optically-excited mercury vapour causes a brown deposit to form on the inner wall of the resonance tube, which, by absorbing 2636 light, renders the tube very inefficient. This deposit was removed from time to time by polishing the interior of the tube with a small ball of pitch covered with wet rouge on the end of a glass rod. It was found that some lines were not enhanced at all by the nitrogen, while the increase in intensity of the green line was as much as 30-fold. The values found for the different lines are given in the following table :—

Lines.	Intensity Increase.	Lines.	Intensity Increase.
5461	32-fold.	3131	16-fold.
4358	16 ,,	3125	2 ,,
4046	8 ,,	3021	6 ,,
4077	1 ,,	2967	4 ,,
3663	4 ,,	2894	8 ,,
3654	1 ,,	2753	16 ,,
3650	16 ,,	2652	2 ,,
3341	5 ,,	2653	10 ,,

It was of the utmost importance to ascertain, if possible, the action of the nitrogen in producing this enormous increase in the radiation of the mercury vapour. The hypothesis was made that it produced an increase in the absorption of the light, and the hypothesis was tested in the following way :—

A quartz tube 10 cm. long, closed with flat end-plates

Fig. 3.
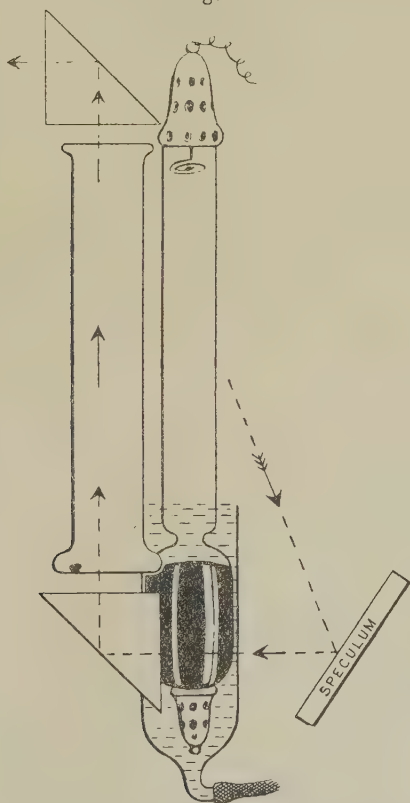
fused on, was mounted as close as possible to the water-cooled mercury arc. Two right-angle prisms of quartz were arranged as shown in fig. 3, and a small plane mirror of speculum metal mounted at such an angle as to reflect the light of the arc into the lower prism, from which it eventually reached the spectroscope, after traversing the vertical tube. The tube contained a drop of mercury and was connected to the pump and nitrogen bulb. By interposing

a sheet of glass between the lamp and the absorption tube
the mercury vapour can be changed from the excited to the
normal condition. A series of spectra of the mercury-arc
light, after transmission through the absorption tube, were
made with different exposure times, both with and without
the glass plate. The most casual examination showed that
the 4046 line was very powerfully absorbed by the excited
mercury vapour with a pressure of 3 mm. of nitrogen in the
tube. (This line should not be absorbed at all according to
the diagram of orbits.) Comparison of the spectra showed
that the arc line had been reduced to less than 25 per
cent. of its normal value by passage of the light through a
layer of excited mercury vapour at room temperature 6 cm.
in thickness in an atmosphere of nitrogen at 3 mm. pressure.
This indicates that something happens as the result of the
presence of nitrogen, which is equivalent to bringing elec-
trons to the $2p_3$ orbit in an enormous number of the atoms.
We should therefore expect strong absorption for all lines
produced by the fall of electrons to this orbit. This was
found to be the case, the lines 2752·8, 2967, and 2534·7
being greatly reduced in intensity, though not to the same
degree as 4046.

The absorption was next investigated with a very fine
Lummer-Gehrke plate of quartz, made by the Hilger Com-
pany. Even with the high resolving power of this instrument
no trace of reversal could be detected on the spectrograms
for any of the lines (except 2536), in the case of mercury *in
vacuo*, but the presence of a fraction of a millimetre of
nitrogen caused the reversal of the 4046 line, while
with nitrogen at 5 mm. the reversal was so strong as to
nearly obliterate the line. With increasing nitrogen pres-
sure the reversal becomes less powerful and the line increases
in intensity. These effects are shown as negatives on
Pl. XXV. (fig. 4), *a* vacuum, *b* nitrogen. The interference
system was projected on the slit of the spectrograph, with
a slit width such that the lines 4046 and 4077 were in
contact. These broadened lines are traversed by the hori-
zontal interference bands in which the absorption shows as a
reversal or horizontal bright band (in the negative repro-
duced) bisecting the dark band. The appearance of the lines
with the mercury *in vacuo* is shown on Pl. XXV. (fig. 4 *a*)
and in nitrogen at 3 mm. by *b*. The strong enhancement of
line 3131 with respect to 3125 is shown on the same plate
(fig. 3 *a* & *b*). (Upper spectrogram mercury *in vacuo*, lower,
in nitrogen at 3 mm.) The appearance of the 5650–3663
group is similar to that shown in fig. 1 *f*.

The relative intensities of the $2p$–ms lines (5461, 4358, and 4046) are the same in the optically-excited mercury *in vacuo* and in the arc (ratio $4:2:1$). The introduction of nitrogen alters this ratio to $128:32:4$—that is, the green line is now 32 times as intense as the violet line 4046, instead of four times as intense. Interpreting this by orbital transfers alone, we should be obliged to conclude that the subsequent behaviour of electrons raised to the $2s$ level depended upon whether they were brought there by the absorption of 4046 from $2p_3$ (as would seem to be the case with mercury atoms in nitrogen), or by absorption of 4358 from $2p_2$, as when the mercury is *in vacuo*. In the former case a much larger number (relatively) fall back to $2p_1$ (giving 5461 emission) than in the latter.

In view of more recent results, however, it is my opinion that we are not justified in trying to explain these results as above outlined. With a chlorine filter which cuts out 2967, 3125, and 3131 from the exciting light, we obtain 2967 and 3131 at great intensity, if air is in the resonance tube at a pressure of only 0·04 mm.; with a bromine filter, which removes 4046 and 4358 from the exciting light, we find these lines strongly developed in the spectrum of the optically-excited vapour, if nitrogen is present. These frequencies are apparently excited by the nitrogen after it has been excited by the optically-excited mercury. That some such effect comes into play is rendered extremely probable in view of the results obtained by Lord Rayleigh with active nitrogen as an exciter of the mercury spectrum and the more recent work of Foote and Mohler, who also found that nitrogen, activated by the electric discharge, was able to develop the mercury spectrum by mere contact with the vapour. Their experiment was made by subjecting a mixture of nitrogen and air to an intermittent discharge and photographing the spectrum of the after-glow, during the time-intervals of no electrical excitation.

There is another possible factor which may modify the intensity ratios—namely, absorption in the resonance tube. The optically-excited vapour is photographed "end-on," the length of the luminous column being about the same as that of a column of optically-excited vapour in nitrogen used for the demonstration of the powerful absorption of 4046. This same absorption must also operate on the 4046 radiations emitted by the lower layers of vapour in the resonance tube, and thus reduce the observed intensity of the line.

If a considerable absorption (though less) existed for 4353, and practically no absorption for 5461, we might have the

observed change of intensity ratios as a result of *absorption alone*. This point will be examined experimentally by limiting the illuminated region of vapour to a thin sheet, under which condition absorption by excited vapour will be practically eliminated.

In the earlier paper I have recorded the circumstance that other gases behave in a manner different from that of nitrogen, some of the lines being *decreased* in intensity, others increased. The effects found with carbon monoxide at 0·22 mm. and helium at 5 mm. are given in the following tables:—

CARBON MONOXIDE.			HELIUM.		
Intensity Increased.	Intensity Decreased.	No Change.	Intensity Increased.	Intensity Decreased.	No Change.
4358	4077		4358	3654	4077
4046		3021	4046	3663 slightly.	3341
3341 slightly.	3663	3023	3650	3125	3131
3131	3654		3021	3023	2967
2967 5-fold.	3650		2653 ⎱ slightly.	2652	2894
2894 slightly.	3125		2655 ⎰		
2653 5-fold.	2652		2536 greatly.		

The most striking case of altered intensity ratios occurred in the case in which the thin quartz cell, usually used for bromine, was filled with chlorine and used as a filter. This filter gave a slight transmission of the 3131 region of the spectrum, so the optically-excited spectrum showed traces of most of the lines observed without a filter. The introduction of air at a pressure of 0·04 mm. caused the following changes of intensity:—

2536 reduced $\frac{1}{2}$.
2652   ,,   ,,
2653 increased 5-fold.
2894   ,,   2   ,,
2967   ,,   16   ,,
3021 no change.
3125 reduced $\frac{1}{4}$.

3131 increased 16-fold.
3650 reduced $\frac{1}{3}$.
3663 increased 2-fold.
4046   ,,   ,,
4047 reduced $\frac{1}{2}$.
4358 increased 2-fold.

The resulting spectrum shows 2967, 3131, 4046, and 4358 at very great intensity with the other lines extremely weak, 3125 scarcely visible, in fact.

With a bromine filter the actual intensities of some of the

OOD.

Phil. Mag. Ser. 6, Vol. 50, Pl. XXV.
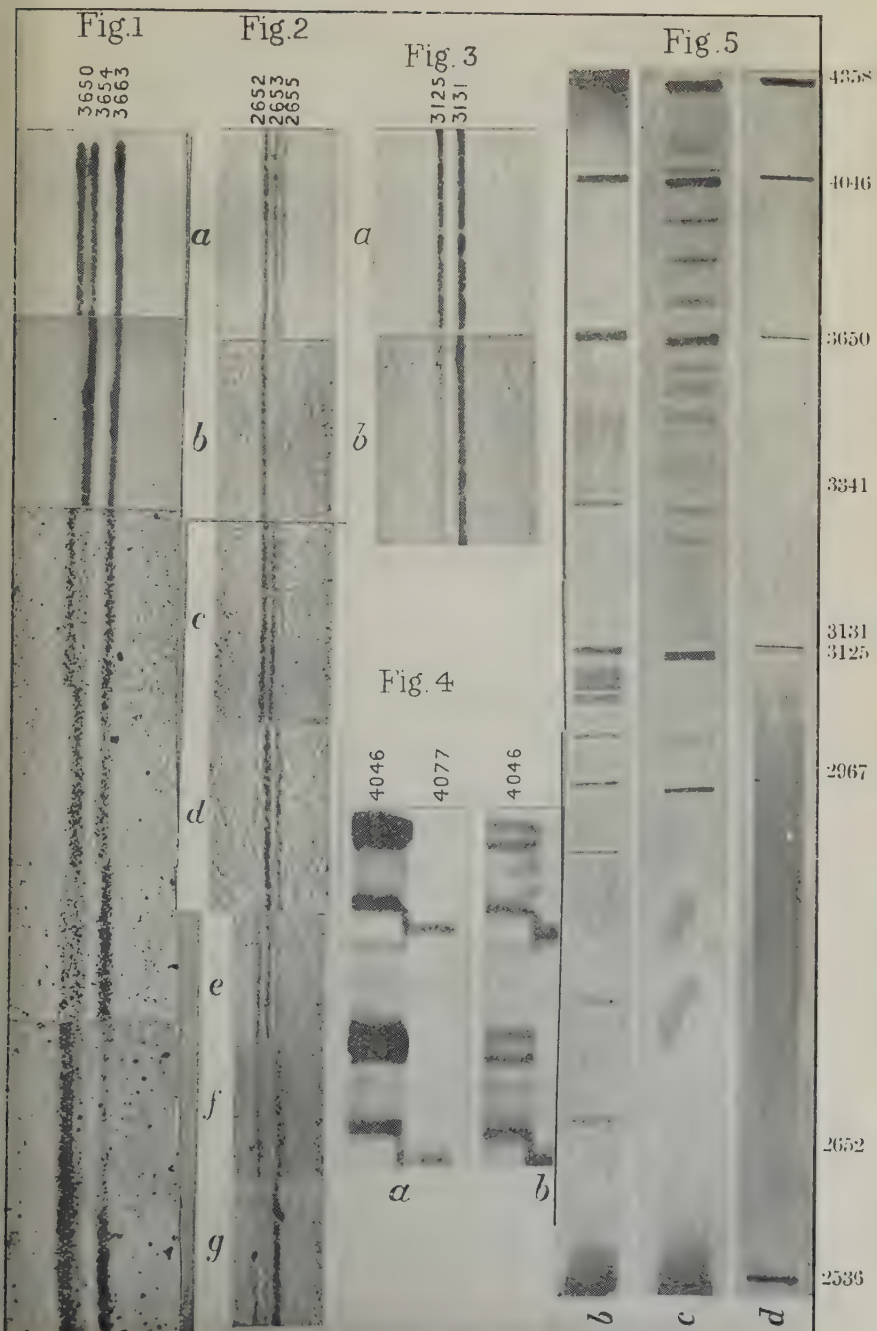
principal lines with the mercury *in vacuo* and in nitrogen at 8 mm. were as follows :—

Line	2967.	3125.	3131.	3650.	3654.	3663.
Int. *in vac.*	1	1	2	0	0·5	0·5
Int. in N_2	2	0·5	4	2	0·25	1

With the bromine filter and air at ·04 mm. the enhancements were as follows :—2967 twenty-fold, 3125 reduced one-half, 3131 two-fold, 3650 developed from 0, 3654 reduced one-half, 3663 two-fold increment.

That radiations corresponding to electron falls from the D levels are developed by the admixture of a foreign gas has been shown for the 4D orbit, though not as yet for the 3D.

The lines 2652 and 2653, originating from $2d'$ and $2d''$ and corresponding to 3125 and 3131 of the d and d'' levels, are shown in the photographs clearly separated from 2655, the line originating on the 4D orbit.

These three lines, as they appear in the arc spectrum, are shown on Pl. XXV. (fig. 2 *a*). In the case of the optically-excited vapour *in vacuo*, only 2652 appears (fig. 2 *b*) ; whereas under similar conditions the corresponding lines 3125 and 3131 both appear, the latter having the greater intensity. With ·03 mm. of air in the tube, 3653 develops with an intensity equal to that of 2652 (fig. 2 *c*). With nitrogen at 1 cm., 2652 has faded, 2653 has increased, and 2655 develops (fig. 2 *d*). With helium at 5 mm., 2652 and 2653 are equal, with 2655 faint (fig. 2 *e*) ; with helium at 7 cm. and 14 cm. we have the changes shown in fig. 2 *f* and *g*, the $2d'd''$ lines fading away and 2655, the 4D line, developing strongly. These effects show the importance of studying the radiations originating on 3D.

Many other observations have been made, but it does not appear to be worth while to discuss them until they have been repeated under conditions which will permit of distinguishing the radiations originating on 3D from those originating on d''. This can be done with the large Lummer and Gehrke quartz interferometer. The resonance tube will be joined to the pump with a Y-tube, which will permit of closing it off from the pump by a rising column of mercury instead of a stop-cock. This will not only obviate the contaminations caused by grease, but will permit more rapid exhaustion and, in consequence, a higher vacuum. The evolution of water-vapour under the illumination is very rapid, and it is quite possible that all of the results obtained up to the present time have been made with water-vapour at very low pressure present in the tube.

3 F 2

There appear to be two, or possibly three, distinct effects produced by the admixture of a foreign gas:—The apparent accumulation of electrons on the metastable orbit $2p_3$ in a very large number of atoms, resulting in the very powerful absorption of the lines which terminate on this orbit and the enhancement of these lines in the optically-excited spectrum. The emission of lines in the optically-excited spectrum which are not present in the exciting light, and which cannot be accounted for by the diagram (fig. 1); this I have provisionally ascribed to the excitation of the mercury spectrum by nitrogen which has been brought into the excited condition by the excited mercury. There seems also to be a third effect which manifests itself as a change in the intensity ratios of the lines produced by the presence of gases at extremely low pressures, of the order of ·01 mm. I have, at the present time, no theory in regard to this last effect.

An effort will be made, in continuing the investigation, to devise some means of studying these actions more precisely and perhaps separating them.

Chamonix,
    July 15th, 1925.

LXXXIII. *The Spectrum of Potassium at Low Voltages.*   *By* F. H NEWMAN, *D.Sc., A.R.C.S., Professor of Physics in the University College of the South-West of England, Exeter* *.

[Plate XXVI.]

1. *Introduction.*

EXPERIMENTS show that collisions between an atomic system and a free electron may cause the system to pass from the normal state of least energy to a stationary state of greater energy. Accordingly the electron would lose an amount of energy and undergo a diminution in its velocity corresponding to the energy difference between the second and the first state of the system; but such collisions can occur only when the energy of the free electron is greater than that energy difference. In a previous paper †

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the author has shown that on the basis of this theory the normal operation of an arc below ionization potential should result in a line-by-line spectrum corresponding to changes of orbit involving less energy than the ionization potential.

It must be remembered, however, that the valency electron within an atom may be displaced to various stationary states by other processes. As pointed out by Klein and Rosseland *, the consequence of energy-loss by the impacting electron would be, apparently, a disturbance of the temperature equilibrium of a mixture of atomic systems and free electrons, since some atoms would acquire temporarily higher energy, whilst the electrons lose energy. This would contradict the second law, and, accordingly, the transition must be compensated for by the free electrons themselves as soon as their velocities are distributed according to the temperature equilibrium. Such collisions then can occur also between free electrons and atoms, in which the atom bombarded passes without emitting radiation from a stationary state of greater energy into a stationary state of smaller energy, while the impacting electron acquires an amount of kinetic energy equal to the energy lost by the atom. These collisions are termed of the "second order." In addition, the excited atom colliding with neighbouring atoms would displace the valency electron in the latter.

Absorption and fluorescence phenomena indicate that the electron can be displaced directly from its normal stationary state to any of the $m\pi$ orbits, and it is to be expected that similar displacements would be produced by electronic bombardment. Photographic observations made by the author with sodium vapour showed the development of the spectrum in the order of the potentials predicted by theory. A three-electrode discharge-tube was used, and electrons emitted from a heated tungsten-wire cathode were accelerated by a potential difference applied between the grid and the cathode, and entered a force-free space between the grid and anode. It was found necessary to focus light from the immediate neighbourhood of the grid on the spectrograph, as it was only at this part of the discharge-tube that the impacting electron energy was not lowered by the negative space-charge effect. The excitation of the potassium spectrum below ionization potential was observed in a similar manner, and the results obtained are described below.

The emission of the doublet λ 5896, 5890 when sodium vapour is bombarded with electrons of energy less than that

corresponding to the ionization potential of sodium vapour—5·12 volts—has been noted by various observers [*], but the appearance of the corresponding pair—λ 7699, 7665—in the principal series of potassium below the ionization potential of potassium vapour is not so well known, although Foote, Meggers, and Mohler [†], using a discharge-tube in which the grid—a helical coil—was mounted extremely close to the tungsten hot-wire cathode and in metallic contact with a concentric hollow cylinder, have excited this doublet at potentials below 4·32 volts, the lowest potential at which it appeared being 1·60 volts. No more lines were observed until the accelerating field reached 4·32 volts, at which the entire arc spectrum was excited. In addition, these experimenters photographed the doublet λ 4642·2, 4641·6, the emission of which represents interorbital movements where

Fig. 1.

Graphical representation of Potassium Atom.
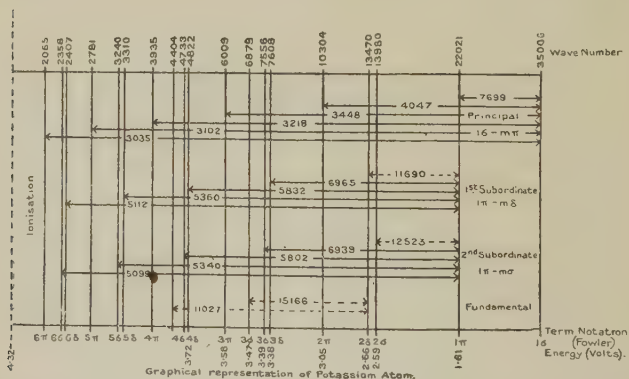
the change in azimuthal quantum number is, according to Sommerfeld, 2 units and should be precluded by the selection principle. The presence of these lines cannot be attributed to the incipient Stark effect, as in these experiments no field was applied between the grid and the plate ; but it may be explained by the interaction of atomic fields of neighbouring positive ions and electrons, which fields may be many times greater than the intensity of the applied external electric field.

A graphical representation of the energy levels in the potassium atom is shown in fig. 1. The nucleus is supposed situated away to the right of the diagram, and the vertical

* Wood and Okano, Phil. Mag. xxxiv. p. 177 (1917) ; Foot, Meggers, and Mohler, Astrophys. Journ. lv. p. 145 (1922).

† *Loc. cit.*

lines represent non-radiating orbits, the wave-numbers corresponding to any particular orbit being shown against the line. Transitions from the $m\pi$ orbits to the 1σ orbit yield lines of the principal series, the first doublet of which is excited when the electron passes from the 1π to the 1σ orbit, and the difference in wave-numbers, corresponding to the initial and final states, gives directly the wave-number of the radiation emitted. All of the $m\pi$ orbits are really double, but their separation is indistinguishable on the small scale of wave-numbers. The first line of the first subordinate series is given by an electron falling from the 2δ ring to the 1π ring, and the other lines of this series correspond to movements from the $m\delta$ orbits to the 1π orbit. In a similar manner transitions from the $m\sigma$ orbits to the state represented by 1π yield the second subordinate series lines, and falls from the $m\phi$ to the 2δ orbits give the fundamental series lines. The various combination lines can be considered in the same way. In all cases the horizontal lines extending between orbits show the wave-length of the radiation emitted by energy transitions between the orbits, the dotted lines indicating wave-lengths falling outside the range of sensitiveness of the plate. As the selection principle allows only those changes in which the azimuthal quantum number changes by unity, and as the numbers for the $m\sigma$, $m\pi$, $m\delta$, and the $m\phi$ orbits are, respectively, 1, 2, 3, and 4, interorbital movements from the $m\pi$ to the $m\sigma$ or the $m\delta$ levels are permitted, but transitions from the $m\sigma$ to the $m\delta$ orbits are precluded.

The energy level of any particular state can be expressed also in terms of the potential difference through which the bombarding electron must fall, in order to accumulate kinetic energy equivalent to a quantum of radiation of wave-number ν; and for comparison with the results of experiments on ionization the work necessary to remove the electron within the atom from one orbit to another is most conveniently expressed in terms of equivalent volts by putting $W_1 - W_0 = eV$, where V is the potential difference through which the bombarding electron must fall to acquire the corresponding amount of energy, W_1 and W_0 being the energies in the two states. Utilizing the quantum relation $hc^2\nu = eV . 10^8$, we can express the wave-number in terms of the potential difference by

$$V = \frac{\nu}{8102}.$$

It is convenient to consider the work required to displace

the electron from an inner to an outer orbit, and hence to the innermost orbit is ascribed zero energy. To displace the electron to infinity from this orbit, energy equivalent to 4·32 volts is required. In a similar manner 1·61 volts shown at the 1π ring does not represent the energy of this particular state, but is the energy which a bombarding electron must possess to displace the valency electron from the 1σ to the 1π orbits. This corresponds to the resonance potential of potassium vapour, and if the electron, after displacement to the 1π orbit, returns to the 1σ state, the quantum of energy eV received at bombardment is given up as a quantum of radiant energy $h\nu$ of wave-number ν. Collisions with electrons of 3·05 volts energy should result in a maximum displacement of the valency electron to the 2π state ; and as there seems to be no reason to suppose that an electron at collision should transfer all of its energy to the atom, electrons of 3·05 volts should eject the electron within the atom to the 1σ, 2σ, or the 2δ orbit, in addition to the 2π orbit, in different atoms. It is to be expected, therefore, that if potassium vapour is bombarded with electrons of this energy, radiation of $\lambda\,7699$, 7665, $\lambda\,12523$, 12434, $\lambda\,11772$, 11690, and $\lambda\,4047$, 4044 should be emitted by interorbital transfers permitted by the selection principle. In a similar manner other lines of the various series should be excited step-by-step as the accelerating potential is increased, until, when the ionization potential is attained, the entire arc spectrum should appear.

2. *Experiments.*

The form of discharge-tube used was similar to that described in the previous paper. Electrons emitted from three short tungsten wires, arranged in parallel, were accelerated by an electric field applied across a nickel gauze grid and the cathode, and entered a force-free space between the grid and a nickel cylinder which completely surrounded the cathode. The whole tube, containing a small quantity of distilled potassium metal, was placed inside an electric furnace, and by properly regulating the temperature of the potassium vapour a vapour pressure was maintained for which relatively few electron-atomic collisions occurred over the short accelerating field between the cathode and the grid, and the majority of the electrons passing into the relatively large force-free space had, at the instant of collision, a velocity corresponding to the impressed field.

Throughout the experiments the discharge-tube was con-
tinuously exhausted and the residual gas-pressure maintained
at 10^{-3} mm. of mercury. The furnace temperature was
245° C., approximately, at which the potassium-vapour
pressure is about 0·1 mm. of mercury *. As the space-
charge effect lowers the impacting electron energy, except
in the immediate neighbourhood of the grid, it was necessary
to focus on the slit of the quartz spectrograph light coming
from this part of the tube. Special rapid panchromatic
plates were used for all exposures, but they were not very
sensitive to the doublet λ7699, 7665. Accordingly, the plate
was sensitized by treatment with a dicyanin solution, the
formula for which was kindly supplied by Messrs. Ilford.
This gave satisfactory results.

The measured potential difference applied between the
grid and the cathode was not the actual energy of the bom-
barding electrons, and the readings were corrected for errors
due to contact potential, potential fall along the lead-in
wires and the filament, and the initial velocity of the electrons
emitted from the cathode. These errors were determined by
measuring the ionization potential of the vapour and com-
paring the experimental and theoretical values. The mean
of a series of readings gave 4·1 volts, and, as the calculated
value is 4·32 volts, the correction 0·3 volt has been made in
all the measurements quoted.

The radiation first appeared in close proximity to the grid
and was red in colour, but as the accelerating voltage was
raised, the radiation changed to the characteristic violet
colour associated with luminous potassium vapour, and at
the ionization potential filled the space between the grid and
the anode. The spectrum lines excited at different voltages
are given in Table I. and the spectrograms in Pl. XXVI.

The first doublet of the principal series appeared at
1·9 volts, in fair agreement with the calculated energy
1·61 volts, which the impacting electrons should have to
displace the valency electron from the 1σ to the 1π orbit;
but the intensity of the radiation was very feeble, and ex-
posures of approximately 40 hours were required. According
to the energy-level diagram, λ 12434, 12523 should appear
next above 2·59 volts, followed by λ 11690, 11772 at
2·56 volts; but both of these doublets, lying in the infra-red,
are far beyond the range of the plate, so that with accelerating
potentials of 3·0 volts, only the first member of the principal

* Hackspill, *Comptes Rendus*, cliv. p. 877 (1912).

series should appear on the plate   This is shown in the first spectrogram.

TABLE I.

Potassium Lines excited at various Applied Potentials.

Series.	Wave-length.	Excitation voltage.	
		Experimental.	Calculated.
$1\sigma - 1\pi$	λ 7665 λ 7699	1·9 volts.	1·61 volts.
$1\pi - 2\sigma$	λ 12434 λ 12523	—	2·59
$1\pi - 2\delta$	λ 11690 λ 11772	—	2·66
$1\sigma - 2\pi$	λ 4044 λ 4047	3·3	3·05
$1\pi - 3\delta$	λ 6936 λ 6965	3·7	3·38
$1\pi - 3\sigma$	λ 6911 λ 6939	3·7	3·39
$1\sigma - 3\pi$	λ 3447 λ 3448	3·9	3·58
Complete arc spectrum		4·4	4·32

The second member of this series should be excited when the impacting energy is equivalent to 3·05 volts, and, as shown in spectrogram No. II., λ 4044, 4047 were emitted at 3·3 volts. At 3·7 volts, λ 6911, 6939, 6936, and 6965 appeared, but the dispersion of the spectrograph is too small to show resolution (spectrogram No. III.).

At 3·9 volts the third doublet of the principal series—λ 3447, 3448—was emitted and photographed in spectrogram No. IV. At 4·4 volts the entire arc spectrum resulted as shown in spectrogram No. V. With the exposures used no additional lines were observed between 3·9 and 4·4 volts; but in any case it would be difficult to get sharp differentiation between the different lines in this range, for it is likely that the probability of excitation of any particular line increases for a short range as the corresponding voltage is exceeded.

The photographic observations indicate that displacements of the valency electron from the normal state—1σ—to a

The spectrum of Potassium at low voltages.
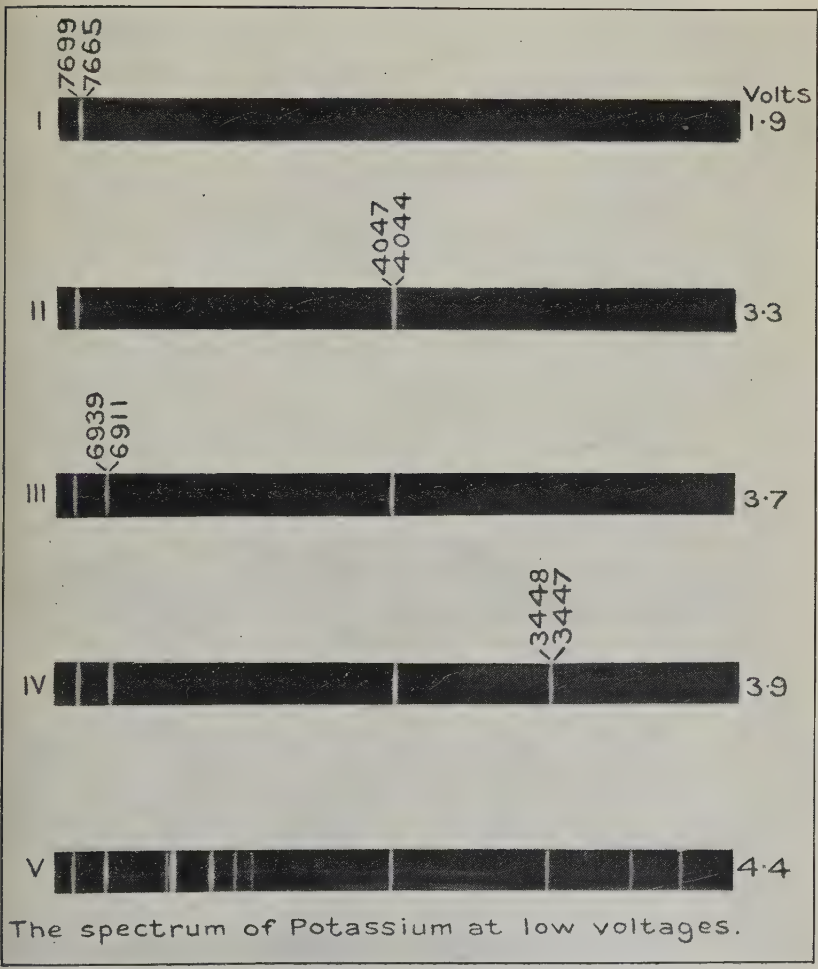
second state represented by $m\pi$ can take place at electronic collision, if the impacting energy is greater than that corresponding to the second state. A step-by-step emission results as the energy of the bombarding electrons is raised to a value slightly exceeding that calculated from the quantum relation.

LXXXIV. *On the Derivation of Planck's Law from Einstein's Equation. By* A. S. EDDINGTON, *F.R.S.**

1. IT is generally considered that Einstein's investigation in *Physikalische Zeitschrift*, xviii. p. 121 (1917) gives the clearest insight into the origin of Planck's law of radiation. The argument is surprisingly elementary, and the investigation is self-contained except for two results assumed to be already known, viz. Wien's displacement-law and Boltzmann's formula for the relative numbers of systems in different states of energy in an assemblage at given temperature.

It does not seem to be generally known that it is unnecessary to assume Boltzmann's formula ; this, as well as Planck's law, can be deduced directly from Einstein's equation. It seems advantageous to make this modification in the proof so as to cut out reference to a difficult extraneous investigation. We have then the security that no assumptions are made other than those plainly brought before us ; and the remarkable force and comprehensiveness of Einstein's method is more fully displayed.

The deduction of Planck's law without assuming Boltzmann's formula is given here. Familiar ground is traversed in § 2 ; the modification begins in § 3.

2. Consider two states of an atom with internal energy χ_1, χ_2 respectively $(\chi_2 > \chi_1)$. The atom can pass from state 2 to state 1 by emitting radiation of energy $\chi_2 - \chi_1$, and the reverse process is a passage from state 1 to state 2 with absorption of a like amount of radiant energy. By the quantum law the radiation emitted or absorbed is of frequency ν_{12}, given by

$$h\nu_{12} = \chi_2 - \chi_1. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

By the principle of independent balancing the number of passages in the two directions in matter in thermodynamical equilibrium will balance independently of any other processes of transition to or from states 1 and 2.

According to Bohr's theory of the atom, the possible values of χ form a discontinuous series ; but we make no use of this except to justify a verbal abbreviation, viz. that we can speak of the number of atoms of energy χ instead of the number in a range χ to $\chi + d\chi$.

Let n_1, n_2 be the number of atoms in states 1 and 2, and $I(\nu_{12})$ the energy-density of radiation of frequency ν_{12}. At present we do not assume equilibrium. Then, for the reasons explained by Einstein, the number of transitions in the two directions in time dt is set equal to

$$1 \to 2 \qquad a_{12}\, n_1\, I(\nu_{12})\, dt,$$

$$2 \to 1 \qquad b_{21}\, n_2\, dt + a_{21}\, n_2\, I(\nu_{12})\, dt,$$

where the atomic constants a_{12}, b_{21}, a_{21} are independent of temperature. No assumption is made as to whether a_{21} is positive or negative.

Apply this to an assemblage in equilibrium at temperature T. The balancing of direct and reverse processes gives Einstein's equation

$$a_{12}\, n_1\, I(\nu_{12}, T) = b_{21}\, n_2 + a_{21}\, n_2\, I(\nu_{12}, T), \quad . \quad . \quad (2)$$

where I is no longer arbitrary, but represents the distribution-law of radiation at temperature T.

From (2)

$$\frac{n_1}{n_2} = \frac{a_{21}}{a_{12}}\left(1 + \frac{b_{21}}{a_{21}\, I(\nu_{12}, T)}\right). \quad . \quad . \quad . \quad (3)$$

3. We now consider a third state of energy χ_3 $(\chi_3 > \chi_2 > \chi_1)$. Then, since

$$\frac{n_1}{n_2} \cdot \frac{n_2}{n_3} = \frac{n_1}{n_3},$$

we have by (3)

$$\frac{a_{21}}{a_{12}}\left(1 + \frac{b_{21}}{a_{21}\, I(\nu_{12}, T)}\right) \frac{a_{32}}{a_{23}}\left(1 + \frac{b_{32}}{a_{32}\, I(\nu_{23}, T)}\right)$$
$$= \frac{a_{31}}{a_{13}}\left(1 + \frac{b_{31}}{a_{31}\, I(\nu_{13}, T)}\right). \quad (4)$$

This holds for all temperatures T, and T only occurs in (4) in the way indicated explicitly by the notation. We assume

that for fixed value of ν, $I(\nu, T)$ increases without limit as T increases, so that $I(\nu, \infty) = \infty$ [*]. Hence, taking T infinite, (4) gives

$$\frac{a_{21}}{a_{12}} \frac{a_{32}}{a_{23}} = \frac{a_{31}}{a_{13}}. \quad \cdots \quad \cdots \quad (5)$$

By (4) and (5)

$$\left(1 + \frac{b_{21}}{a_{21} I(\nu_{12}, T)}\right)\left(1 + \frac{b_{32}}{a_{32} I(\nu_{23}, T)}\right) = \left(1 + \frac{b_{31}}{a_{31} I(\nu_{13}, T)}\right). \quad (6)$$

Introducing now Wien's displacement-law, viz.

$$I(\nu, T) = \nu^3 f(\nu/T), \quad \cdots \quad \cdots \quad (7)$$

where f is an unknown function, and writing

$$c_{12} = b_{21}/a_{21} \nu_{12}{}^3, \text{ etc.}, \quad \cdots \quad \cdots \quad (8)$$

we have from (6)

$$\left(1 + \frac{c_{12}}{f(\nu_{12}/T)}\right)\left(1 + \frac{c_{23}}{f(\nu_{23}/T)}\right) = \left(1 + \frac{c_{13}}{f(\nu_{13}/T)}\right). \quad \cdot \quad (9)$$

Also by (1)

$$\nu_{13} = \nu_{12} + \nu_{23}.$$

4. We notice that (9) presents a strong similarity to the equation satisfied by the exponential function

$$F(\alpha) \, F(\beta) = F(\alpha + \beta) \, ;$$

and it suggests itself that (9) can only be satisfied if each bracket represents an exponential function of ν_{12}/T, etc. The first step is to show that

$$c_{12} = c_{23} = c_{13} = C,$$

C being an absolute natural constant. Equation (9) may be written

$$\frac{1}{f(\nu_{12}/T)} \cdot \frac{1}{c_{23}} + \frac{1}{f(\nu_{23}/T)} \cdot \frac{1}{c_{12}} - \frac{1}{f(\nu_{12}/T + \nu_{23}/T)} \cdot \frac{c_{13}}{c_{12} c_{23}}$$
$$= -\frac{1}{f(\nu_{12}/T) \, f(\nu_{23}/T)}.$$

Write this three times, taking T equal to three temperatures, T_1, T_2, T_3 successively. Eliminate $1/c_{23}$ and $c_{13}/c_{12} c_{23}$ between the three equations. We thus find $1/c_{12}$ equal to an expression made up of functions of six arguments,

$$\nu_{12}/T_1, \quad \nu_{12}/T_2, \quad \nu_{12}/T_3, \quad \nu_{23}/T_1, \quad \nu_{23}/T_2, \quad \nu_{23}/T_3.$$

[*] This is also assumed by Einstein; the assumption is discussed in § 6.

These reduce to four independent arguments,

$$\nu_{23}/T_1, \quad \nu_{23}/T_2, \quad \nu_{23}/T_3, \quad \nu_{23}/\nu_{12}.$$

Now, c_{12} can only depend on the states 1 and 2, and therefore it cannot depend on any of the above four arguments. Hence it must be a constant (involved in the universal function f). Equation (9) accordingly becomes

$$\left(1 + \frac{C}{f(\alpha)}\right)\left(1 + \frac{C}{f(\beta)}\right) = \left(1 + \frac{C}{f(\alpha + \beta)}\right), \quad . \quad (10)$$

where $\alpha = \nu_{12}/T, \quad \beta = \nu_{23}/T$.

It is well known that the only solution of (10) is the exponential function. Thus

$$1 + C/f(\alpha) = e^{k\alpha}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

so that

$$f(\alpha) = \frac{C}{e^{k\alpha} - 1}.$$

Hence by (7)

$$I(\nu, T) = \frac{C\nu^3}{e^{h\nu/RT} - 1}, \quad . \quad . \quad . \quad (12)$$

where we have written $k = h/R$. Equation (12) is Planck's law.

Also by (3)

$$\begin{aligned}
\frac{n_1}{n_2} &= \frac{a_{21}}{a_{12}}\left(1 + \frac{b_{21}}{a_{21}\,\nu_{12}^3 f(\nu_{12}/T)}\right) \\
&= \frac{a_{21}}{a_{12}}\left(1 + \frac{C}{f(\nu_{12}/T)}\right) \qquad \text{by (8)} \\
&= \frac{a_{21}}{a_{12}}\, e^{k\nu_{12}/T} \qquad\qquad \text{by (11)} \\
&= \frac{a_{21}}{a_{12}}\, e^{(\chi_2 - \chi_1)/RT}. \quad . \quad . \quad . \quad . \quad . \quad (13)
\end{aligned}$$

If q_1/q_2 is the limit of n_1/n_2 when T is infinite, we have by (13)

$$q_1/q_2 = a_{21}/a_{12}.$$

Hence

$$n_1 : n_2 = q_1\, e^{-\chi_1/RT} : q_2\, e^{-\chi_2/RT}, \quad . \quad . \quad (14)$$

which is Boltzmann's formula assumed by Einstein, but here derived as a consequence of his equation.

5. The argument applies to ionization (χ_2 positive) as well as excitation (χ_2 negative), so that (14) applies to the calculation of the number of free electrons of given energy. We thus obtain a partial proof of Maxwell's law for free electrons

(*partial*, because the weight-factor q_2 is not evaluated in this investigation). A similar proof applies to the velocity-distribution of atoms if we may assume that atoms are (occasionally) dissociated from molecules by absorption of radiation. Alternatively Maxwell's law for atoms and molecules follows from Maxwell's law for electrons by the balancing of direct and reverse processes of interchange of energy between them in radiationless encounters.

The constant R in (12) and (14) can now be identified in terms of the mean kinetic energy of a molecule at given temperature.

It might seem that the derivation of Maxwell's law by this method is shorter and possibly more rigorous than the usual proofs in statistical mechanics ; but it must be remembered that we do not determine the weight factor

$$q = du\, dv\, dw\, dx\, dy\, dz$$

by this argument, and it is essentially the problem of weight which makes the usual proofs long and difficult.

6. We assumed in § 3 that $I(\nu, \infty) = \infty$. It can be shown from the second law of thermodynamics that $\partial I(\nu, T)/\partial T$ is never negative, but it cannot be proved that $I(\nu, T)$ increases without limit. If we do not make this assumption we cannot deduce Planck's law, although Boltzmann's formula is obtained without modification. In that case equation (5) fails, and an additional factor (independent of temperature) accordingly occurs on the right side of (9). Proceeding as before, but with four temperatures instead of three in order to eliminate the additional constant, we can show that

$$c_{12} = c_{23} = c_{13} = C ;$$

and (10) is replaced by

$$\left(1 + \frac{C}{f(\alpha)}\right)\left(1 + \frac{C}{f(\beta)}\right) = \left(1 + \frac{C}{f(0)}\right)\left(1 + \frac{C}{f(\alpha + \beta)}\right).$$

The general solution is

$$1 + C/f(\alpha) = ae^{k\alpha},$$

and hence

$$I(\nu, T) = \frac{C\nu^3}{ae^{h\nu/RT} - 1}. \quad \cdots \quad (15)$$

To justify taking $a = 1$ so as to obtain Planck's law, appeal must be made to different considerations, *e. g.* the correspondence principle. If, and only if, $a = 1$, formula (15) gives

I(ν, T) proportional to T when T is large, so that the classical law of equipartition of energy is approached as a limit.

Boltzmann's formula is arrived at whether $a=1$ or not. It should be remarked that it is established only for assemblages in which the atoms are so far apart as not to interfere with one another in absorbing or emitting radiation. If the absorption or emission of an atom is interfered with by other atoms, the coefficients a_{12}, a_{21}, b_{21} will not be purely atomic constants, but will vary according to the extent of this interference, which in turn will depend on the statistical state of the assemblage, including the temperature.

LXXXV. *The Theory of the Schrot Effect.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

MR. THORNTON FRY has pointed out to me that I have done him an injustice in my comparison of his work with that of Dr. Fürth * ; he courteously leaves it to me to make the necessary correction.

I. Dr. Fürth made no reference to the proposition to which I have drawn attention ; his argument was " based on a mere analogy." Mr. Fry was therefore perfectly right to criticise it on that ground, and was under no obligation to find a support for it from the work of others.

II. My proposition applied to Dr. Fürth's equation of the motion of the system considered does not actually lead either to Dr. Fürth's result or to the more correct result which Mr. Fry has given. The differences are due to the different treatment of small terms of the order R/L. If my proposition is applied to what Mr. Fry holds to be the correct equation of motion, it leads to his result.

III. Mr. Fry has given in equation (10) of his paper a proposition which differs from that to which I drew attention only in being slightly more general. I was wrong therefore in suggesting that his work was not founded on that proposition. On the other hand, his mode of deriving the proposition is quite different. It seems to me rather less stringent and less clearly based on the fundamental physical assumptions ; it was for that reason that I did not immediately recognize it. But this is a matter of opinion in which doubtless Mr. Fry would not agree with me.

NORMAN R. CAMPBELL.

* Phil. Mag. l. p. 81 (1925).

LXXXVI. *Maxwell's Electromagnetic Æther and the Michelson-Morley Experiment. By* A. Press, *Rockefeller Foundation Visiting Professor of Physics, Chulalongkorn University, Bangkok, Siam* *.

Summary.

THE fact that light manifestations according to Maxwell require an ætheric and not a material medium calls for an interpretation of Gladstone and Dale's so-called molecular refractive index m. Such index really refers to the non-material medium of molecular diameter d_m surrounding and attached to the nucleus. It is shown that by coordinating the Gladstone and Dale rule with that of Lorentz and Lorenz that the molecular index m becomes a function of the material density of the medium, and incidentally, therefore, a function of the temperature. Any increased value of m with density is to be ascribed to a further proportional filling up of the intermolecular space with a modified ætheric medium, so that eventually no pure (unmodified) æther exists between the nuclei.

Whereas, however, the intrinsically attached non-material medium moves with the individual nuclei (Bradley aberration effect), relative motion is assumed possible (Fizeau effect) between the molecules of diameter d_m and the modified æther medium filling up the pores between the molecular diameters. Only in this way can one successfully picture critical total reflexion taking place in refractive media. As a consequence, therefore, of the mass action of the Earth producing a filling-up modified æther medium, only relatively null results can follow from experiments of the type of Michelson-Morley or that of Sir Oliver Lodge. In contradistinction due to the mass action of the Sun, it should necessarily follow that an observed bending of the rays should take place due to the modified ætheric atmosphere set up †.

Types of the Æther.

When one refers to the Gladstone and Dale experiments and the establishment of the law as given in Preston's 'Theory of Light,' for example, it is usually stated that there is a molecular refractive index m which is attached to and is a property of the particular molecules of the gas in question.

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* Communicated by Prof. I. J. Schwatt, Ph.D.

† Compare remarks of Dr. L. Silberstein on Prof. D. C. Miller's æther drift experiments, 'Science,' vol. lxi. Supplement, May 22, 1925.

It is with this understanding that we have the relation

$$\mu e = (e - \epsilon) + m\epsilon,$$

where e is the thickness of the plate and ϵ the thickness actually occupied by the molecules *per se*. Thus we have

$$\mu - 1 = \frac{\epsilon}{e}(m - 1). \quad . \quad . \quad . \quad . \quad (1)$$

However, two considerations force one to the conclusion that ϵ/e cannot be the true density. In the first place, since light is an electromagnetic phenomenon it pertains strictly speaking to the æther dielectric, or at least, such modified æther attached to the individual molecules, in the nature of an " atmosphere " as it were, which ordinarily goes under the designation of material dielectric. It is for this embracing and attached ætherial atmosphere that Gladstone and Dale assumed a molecular refractive index m in the above formula. From this point of view, therefore, the real material nucleus of the atom plays but an indirect part. The effective diameter d_m of the atom is in fact the diameter of the embracing material dielectric or modified and attachable æther, if one desires so to designate it.

Determination of Molecular Refractive Index.

To determine the nature of the constant m use can be made of the improved formula of Lorentz, in which we set

$$\frac{\mu^2 - 1}{\mu^2 + 2} = a\rho, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ρ is the material density of the medium and a so far is a constant to be determined. Solving (2) for μ^2 we have

$$\mu^2 = \frac{1 + 2a\rho}{1 - a\rho} \equiv (1 + 2a\rho)(1 + a\rho), \quad . \quad . \quad (3)$$

provided $a\rho$ is negligible in comparison with unity.

On the other hand, from (1) we have

$$\mu^2 = 1 + \left\{ \frac{\epsilon}{e}(m - 1) \right\}^2 + 2\frac{\epsilon}{e}(m - 1) \equiv 1 + 3a\rho + 2a^2\rho^2. \quad (4)$$

If then in (4) we set

$$a = \frac{\epsilon}{e} = n \cdot \frac{\pi}{6} \cdot d_m{}^3, \quad . \quad . \quad . \quad . \quad (5)$$

where d_m is the effective diameter of the dielectric atmosphere of a nucleus and n is the number of molecules per

unit volume, we have

$$m = 1 + \frac{3}{2}\rho \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\frac{\mu - 1}{\rho} = \frac{3}{2} . n . \frac{\pi}{6} . d_m{}^3. \quad . \quad . \quad . \quad (7)$$

The important thing, then, is that the refractive index of the dielectric molecular atmosphere is a function of the density of the gas or liquid (and incidentally of the temperature). This will have important bearing on the elucidation of the Bradley Aberration effect and that of the Fizeau experiment with respect to the Michelson-Morley null observation.

Be it noted that the increase of m with ρ can be attributed to a further deepening of the modified ætheric atmosphere (so called material dielectric) about the material nucleus. Thus, whereas the dielectric atmospheres of free molecules can be conceived of as being due to a " condensation " or adsorption of the æther plenum about the molecule and due to the mass attraction, with greater and greater densities (aggregates of molecules) a pseudo-ætheric atmosphere or ætheric congelation as it were takes place in proportion to the increase in m indicated by (6).

Necessity for a Pseudo-Ætheric Atmosphere for Explanation of Total Reflexion.

That some such action must take place at least in liquids must follow from the consideration that at certain critical angles the waves of light, by the way a purely non-material type of wave motion, are totally reflected without a fair proportion $\left(1 - \frac{\epsilon}{e}\right)$ passing straight through the liquid by way of the pores, as it were. To account for this it must be assumed that due to the mass action (increase in density) of the liquid the pores are substantially filled up with a " congealed " plenum that also moves when the liquid as a whole moves.

The Fizeau versus the Michelson-Morley Experiment.

Whereas, then, in the Fizeau experiment it is possible for the molecularly attached types of atmospheres, of diameters d_m, to move relative to the " congelation " ætheric medium set up, in the case of the Michelson-Morley experiment where no relative motion occurs relatively null results can only be

looked for even in so-called vacuum. This is because the Earth
sets up a congelation effect quite apart from the molecular
density effects of the air molecules. It follows, then, that in
the outer confines of the Earth's atmosphere an ætheric slip
is conceivable. As the greater densities nearer the Earth's
surface are approached, overlapping congelation atmospheres
are encountered till finally the entire light train is carried
forward with the Earth by means of the modified æther.
The null results of Sir Oliver Lodge are then to be
expected and gravitational solar attraction of the light rays
rationalized.

April 5, 1925.

LXXXVII. *On the Nature of the Disturbance in the Second
Medium in Total Reflexion.* By Prof. C. V. RAMAN,
F.R.S., University of Calcutta *.

[Plate XXVII.]

SOME five years ago †, an investigation was carried out in
the author's laboratory of the diffraction phenomena
observed when a pencil of monochromatic light is incident
at slightly less than the critical angle on the boundary
between two media (say, glass and air) and emerges into
the second medium almost grazing the surface. The results
were very interesting and suggestive, and when com-
municating the paper describing them for publication, I had
intended to pursue the matter further and to investigate by
the same methods the cases in which the incidence is made
equal to the critical angle or is increased even further. But
other work intervened and the subject was laid aside.
Sir Arthur Schuster's recent paper on Total Reflexion ‡
recalled the subject to mind, and induced me to make some
further observations. The present paper describes the
experimental facts which are significant enough, and are
fairly easily understood from the point of view adopted in
Dr. Chuckerbutti's paper, but do not seem to fit in with
Sir Arther Schuster's way of looking at the matter.

It is useful briefly to recall Dr. Chuckerbutti's work.
Owing to the enormous dispersion which occurs when light is
incident on a glass-air boundary at or near the critical angle,

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* Communicated by the Author.
† B. N. Chuckerbutti, Proc. Roy. Soc. xcix. A Series, p. 503 (1921).
‡ Proc. Roy. Soc. cvii. A Series, p. 15 (1925).

it is necessary to use highly monochromatic light, *e. g.*, the green or violet line of the mercury arc : the observations are readily made on an ordinary spectrometer. A pencil of light whose aperture is limited by parallel straight edges * passes through a prism of glass, is incident on its second face and emerges nearly grazing the surface. Owing to the narrowness of the emergent pencil, it is considerably spread out by diffraction, and the Fraunhofer pattern seen in the observing telescope shows some remarkable features. It is strongly asymmetrical, the bands on one side of the pattern being wider, fewer in number, and much fainter than the corresponding bands on the other side of the pattern. These features are clearly shown in figs. 1, 2, 3 in Pl. XXVII. which represent the green line of mercury as spread out by diffraction at gradually increasing angles of incidence. In fig. 1 the incidence was at appreciably less than the critical angle, in fig. 2 it was slightly less, while fig. 3 corresponds practically to the case of critical incidence. Panchromatic plates were used, and owing to their comparative insensitiveness to the green rays, long exposures were necessary. Visually, the diffraction bands are broad and quite conspicuous.

When the incidence is increased beyond the critical angle, the principal band in the diffraction-pattern moves out and disappears from the field, followed in succession by one or more of the others accompanying it, but a great many of the long train of bands remain in the field and are just as distinctly visible as ever. Visually with the green of the mercury arc some thirty or forty of the bands may be seen and counted, the particularly astonishing feature being the slowness of the rate at which the intensity in successive bands falls off. For photographing these stages the violet line of the mercury arc and Ilford Zenith plates proved very convenient. Fig. 4 shows the stage at which the incidence is just at the critical angle and the principal band is still visible. In fig. 5 it is at more than the critical angle, and the principal band has moved out of the field altogether, nevertheless the long trail of dark and bright bands in the pattern behind it remains as conspicuous as ever. They can be traced even with angles of incidence considerably in excess of the critical angle.

The phenomena may be explained in the following simple way. If *a* be the aperture of the illuminated surface, *i* the

* As noted by Dr. Chuckerbutti, the place at which the limitation of aperture occurs is not a matter of importance so long as such limitation occurs before actual emergence of the refracted rays from the boundary.

angle of incidence, θ the angle of diffraction, μ the refractive index of glass, the positions of the dark bands in the diffraction pattern are given by the equation tested in Dr. Chuckerbutti's work,

$$Z = \pi a/\lambda \,.\, (\mu \sin i - \sin \theta) = \pm n\pi,$$

where n is an integer. If $\mu \sin i < 1$, both positive and negative values of Z are admissible, but if $\mu \sin i > 1$, which corresponds to the case of "total" reflexion according to geometrical optics, only positive values of Z are possible and correspond to the portion of the diffraction-pattern which continues to be visible.

The rate at which the successive fringes diminish in intensity is certainly far less than in proportion to $\sin^2 Z/Z^2$. An additional factor, namely the increasing width of the diffracted beams as θ alters, has also to be considered as shown by Dr. Chuckerbutti's measurements, and the successive bands should have intensities proportional to $\cos^2 \theta \,.\, \sin^2 Z/Z^2$. This would account for the large number of bands actually seen in the cases of critical incidence and total reflexion.

To find out what was happening in the immediate vicinity of the surface at which "total" reflexion occurs, a microscope placed with its axis nearly parallel to the surface was focussed on it. It was then observed that the two edges of the illuminated area of the surface appeared as extremely fine luminous lines. To focus the front and rear edges, the microscope had, of course, to be in different positions. *Both* the edges were thus found to take part to an equal extent in the observed diffraction effects. Experiment does not thus lend any support to Sir Arthur Schuster's suggestion that one of the edges plays a privileged part in total reflexion phenomena.

Dr. Chuckerbutti in his paper had already pointed out the analogy between the case of refraction by a surface at less than the critical angle and the case of oblique transmission through a plane aperture bounded by straight edges, and Sir Arthur Schuster has based his discussion of total reflexion on an extension of this analogy. The present writer has found experimentally, however, that the analogy breaks down when the incidence in the case of the plane aperture becomes excessively oblique. One of the edges then begins to screen the other from the infalling waves, and the diffraction-pattern becomes excessively feeble and almost disappears when this stage is reached and passed. In the case of total reflexion, however, this is not true, and as observation shows, part of the diffraction-pattern remains visible just as
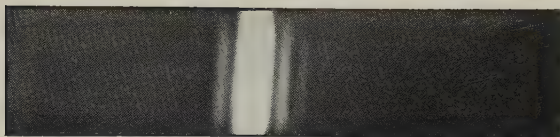
Fig. 1.

Fig. 2.
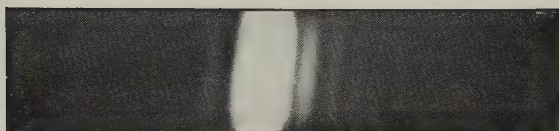
Fig. 3.
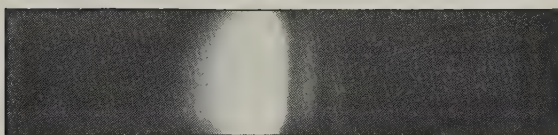
Fig. 4.
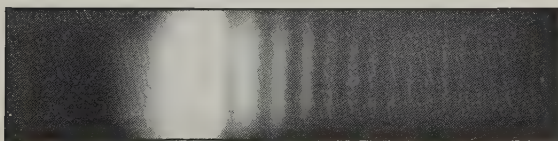
Fig. 5.

Illustrating Total Reflexion Phenomena.

conspicuously as ever. The analogy between the case of total reflexion and that of an aperture in an opaque screen bounded by two straight edges is therefore wholly invalid.

The penetration of the disturbance into the second medium in the case of a beam of finite width illustrated in fig. 5 is also seen conspicuously when, instead of a single aperture, a system of parallel equidistant apertures forming a diffraction-grating limits the incident beam. A long train of diffraction-spectra may then be observed emerging into the second medium, even when the angle of incidence is such that total reflexion should occur according to the laws of geometrical optics. Also, in the case of the Lummer-Gehrcke interfero-meter studied by Dr. Chuckerbutti, I have found that the well-known bands in this instrument can be quite distinctly seen even when the light traversing the plate is incident on its surface at an angle exceeding the critical angle.

Summary.

Photographs have been secured showing the penetration of the disturbance into the second medium which occurs by reason of the limitation of aperture when a pencil of light of finite width is incident at more than the critical angle on the boundary between two media. A long train of diffraction bands can be seen in which the intensity of the successive bands diminishes relatively very slowly. The phenomenon can also be observed in the Lummer Plate. A simple explanation is offered of the results which fit in very well with Dr. Chuckerbutti's earlier work on the case in which the incidence is at less than the critical angle, but do not support the considerations advanced by Schuster.

210 Bowbazaar Street,
    Calcutta, India,
        May 14th, 1925.

LXXXVIII. *On the Circulation Theory of Aeroplane Lift. By* HAROLD JEFFREYS, *M.A., D.Sc., F.R.S.*[*]

IT is well known that when a solid moves through a fluid the resultant force of the fluid on the solid is practically a function only of the size and shape of the solid, its velocity relative to the fluid, and the density of the fluid, provided the velocity exceeds a certain value. This critical

value involves the viscosity of the fluid, but so long as the velocity much exceeds the critical value, the force between the solid and the fluid is substantially independent of the viscosity. It is further known that for bodies of aerofoil form, suitably inclined, the component of the force across the direction of motion is much greater than the component in the direction of motion, owing to the fact that a circulation is set up around the aerofoil.

On the other hand, on the classical theory of the motion of solids through fluids, the solid experiences no resultant force at all when it is moving uniformly. It is therefore usually considered that the existence of a force in such circumstances is a consequence of viscosity, and it appears paradoxical that in a very large class of cases the force is actually found experimentally to be independent of the value of the viscosity. The "cavitation" theory does not help, for the classical solution usually breaks down at velocities far less than are required to give negative pressures on this theory.

It appears to me that to explain the observed facts it is necessary to recognize that the viscous theory differs from the classical theory in two respects, which must be carefully separated. First, the classical theory assumes free slip over the boundaries; viscous theory adopts the experimental fact that there is no slip over the boundaries. Second, in the viscous theory terms of the form $\nu\nabla^2 u$ make their appearance in the equations of motion. They are absent from the equations of the classical theory. The first of these distinctions does not depend on the coefficient of viscosity. Since the observed departure of the facts from the predictions of the classical theory also does not depend on the viscosity, it appears natural to attribute the difference to the former distinction rather than the latter. If this conjecture is correct, fluid resistance in general must be regarded primarily as a consequence of the failure of the classical solution to satisfy the correct boundary conditions, rather than as a direct effect of the viscosity terms in the equations of motion.

Consider first what is likely to happen if we adopt the correct boundary conditions without at the same time taking the viscosity terms into account. The motion produced in the fluid must be irrotational. We know that the irrotational motion of a fluid is completely determinate when the normal velocities over its boundary are given; we know further that this motion as a rule involves slip over the boundaries. Thus in general the correct boundary

conditions will be inconsistent. It appears probable, indeed, that the only type of motion possible will be one where all the solids undergo translation with the same velocity, and none of them has any rotation at all.

The presence of the viscosity terms increases by unity the order of all the equations of motion, and therefore introduces a further arbitrariness into the solution, which makes it possible to satisfy the boundary conditions. Now we know that in a viscous incompressible fluid the vorticity satisfies differential equations of the form

$$\frac{d\zeta}{dt} = \nu\nabla^2\zeta + \xi\frac{\partial w}{\partial x} + \eta\frac{\partial w}{\partial y} + \zeta\frac{\partial w}{\partial z}. \quad . \quad . \quad . \quad (1)$$

If the motion is two-dimensional, two equations of this type become identities, while the third reduces to

$$\frac{d\zeta}{dt} = \nu\nabla^2\zeta. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In either case it is seen that vorticity cannot originate in an element of the fluid entirely surrounded by fluid without vorticity; it must be diffused inwards from the boundary. This diffusion is liable to be a slow process. For instance, consider an aerofoil 200 cm. wide, moving with a velocity of 1000 cm./sec. An element of air takes 0·2 sec. to cross the aerofoil, so that in c. g. s. units $d\zeta/dt$ in the neighbourhood of the aerofoil will be of order 5ζ. Again, ν for air is 0·18 cm.²/sec. If the axis of x be normal to the surface of the aerofoil, much the greatest part of $\nabla^2\zeta$ will arise from $\partial^2\zeta/\partial x^2$. Hence $\partial^2\zeta/\partial x^2$ must be of order 28ζ, indicating that the thickness of the layer with appreciable vorticity is of order 0·2 cm. All air that has not approached the aerofoil within such a distance must be moving irrotationally.

Thus it is a natural consequence of the viscous equations that the motion of the air should be practically irrotational except in a thin layer around the aerofoil and in the wake. On this view, then, it does not appear correct to regard viscosity as responsible for any breakdown of the irrotational theory; it is really a mitigating agent that enables some of the effects of the stringent condition that there must be no slip over a solid boundary to be confined to a comparatively restricted region. The approximate correctness of classical non-viscous hydrodynamics for many problems relating to tides, surface waves, and airships is to be attributed to this fact. In such cases the influence of

viscosity amounts only to a small correction for boundary effects.

In the case of an aeroplane in flight, however, it can be seen that the sharp trailing edge prevents the classical solution from being a good approximation. For in the classical solution there is a stagnation point on the rear surface just above the edge, and fluid must flow round the edge towards it. If this flow were irrotational, it would necessarily imply infinite velocities, and also slip over the boundaries. If the angle within the aerofoil is $\pi - a$, so that the fluid is deviated through a, the ordinary theory for irrotational motion shows that the velocities in the neighbourhood of the edge tend to infinity like $r^{-a/(\pi+a)}$. But in the actual motion the velocities must remain finite ; if further we suppose, what appears reasonable, considering that the relative velocities are zero on the boundary, that they do not vastly exceed those elsewhere, we must abandon the idea that the fluid turns the corner approximately irrotationally. But our earlier argument still shows that fluid at more than a certain small distance from the edge must move almost irrotationally, and if there is a stagnation point on the rear surface the fluid must turn the edge, some of it going fairly near. The only way of avoiding great velocities, therefore, is for the stagnation point to move down till it nearly coincides with the trailing edge ; the necessity for the fluid to turn the corner then disappears. This can be achieved without the motion elsewhere becoming rotational if this motion is cyclic : that is, if a circulation around the aerofoil exists. But the circulation needed to shift the stagnation point to the trailing edge is finite however small the viscosity, and therefore we may expect the main features of the departure from the classical theory to be substantially independent of the viscosity. This agrees with what is observed.

It may happen that the circulation needed to prevent a stagnation point on the rear surface implies greater velocities near the leading edge than are consistent with the maintenance of a steady flow there. In such a case viscosity near the leading edge will form a vortex, and a circulation will be set up in the opposite sense to that required by the trailing edge. No permanent steady motion will then be possible, every vortex detached at one edge upsetting the flow at the other edge and leading to the formation of a vortex there. Thus the detachment of vortices from the two edges alternately is to be expected. This, again, is in agreement with observation.

Summary.

A discussion of the equations of motion of a viscous fluid has shown that vorticity is likely to be small except for fluid that has passed very close to a solid boundary. On the other hand, it appears unlikely that the development of great velocities near a projecting edge, which is inevitable on the classical theory, can take place when we use the correct boundary condition that there is no slip. Non-cyclic irrotational motion in general implies such velocities, and as the motion in most places must be irrotational, it follows that it must be cyclic. The theory appears to account for the main facts concerning the motion of solids through fluid.

St. John's College, Cambridge,
      1925, June 23.

LXXXIX. *A Note on the Spectra of Silicon and Aluminium.* By W. C. McQuarrie, *M.A.*[*]

[Plate XXVIII.]

Silicon.

IN his recent Bakerian Lecture on the spectrum of silicon, Fowler [†] has given an excellent summary of the work to date, including his own extensive investigations. It is noticeable that most of the lines attributed to the neutral atom have not as yet been classified into series. One of the fruitful methods of finding which are the basic series of an element is the study of its absorption spectrum. The investigation of the absorption of silicon vapour presents some special difficulties on account of its high boiling-point and its tendency to react with carbon.

L. and E. Bloch [‡] have recently shown that the important lines in the arc spectra of certain elements may be obtained by observing the absorption produced in the oscillating spark under water.

Metallic silicon is somewhat brittle, and shatters very quickly under the action of a powerful under-water spark. Therefore in the present investigation an alloy of 23 per cent. silicon and 77 per cent. aluminium was used. The method and apparatus have been fully described in a paper by Ireton and Buffam now in the course of publication by the Royal Society of Canada. The only modifications made have been

the substitution of a quenched spark-gap for the open one, and the addition of a second very short gap in parallel with the under-water spark, in order to ensure that the potential difference did not become too great by reason of the eating away of the electrodes.

The spectrum of this alloy observed in this manner showed the same aluminium absorptions as noted by L. and E. Bloch[*]. These were obtained readily with a great variety of conditions. By a careful adjustment of the two spark-gaps, silicon absorptions were also observed. The wave-lengths most easily observed were those constituting the pp' multiplet worked out by Popow[†], namely :

2528·516	....	$1p_1 - 1p_2'$
2524·118	....	$1p_2 - 1p_3'$
2519·210	....	$1p_2 - 1p_2'$
2516·123	....	$1p_1 - 1p_1'$
2514·331	....	$1p_3 - 1p_2'$
2506·659	....	$1p_2 - 1p_1'$

These wave-lengths were not measured, but identified with known values (Fowler[‡]).

As noticed by McLennan and Shaver[§], it is also possible by this method to obtain an absorption at 2881·585 Å., the first member of the sharp series. The conditions for this absorption are less readily attained, and in the present work many plates showed this as an emission line, while the six wave-lengths noted above were absorbed. When the line 2881·585 Å. did appear in absorption, there was also a good deal of emission and the appearance was that of a line asymmetrically reversed.

An effort was also made to observe the multiplet $\lambda\lambda$ 1977–1988 noted by McLennan and Shaver[∥]. The continuous spectrum emitted by the under-water spark is somewhat weak in this neighbourhood, and a prolonged exposure was necessary. The result was a continuous spectrum in the region, with no emission or absorption lines visible.

In the hope of picking out other important lines in the silicon spectrum, the alloy was arced under water with a current of 20 amperes at 220 volts. The spectrum was observed throughout the visible and quartz regions. No silicon absorptions were found, but the spectrum of aluminium was of some interest.

[*] L. and E. Bloch, *loc. cit.*

[†] Popow, *Ann. d. Physik*, xlv. p. 167 (1914).

[‡] Fowler, *loc. cit.*

[§] McLennan and Shaver, Trans. Roy. Soc. of Canada, (3) xxviii. (May 1924).

[∥] McLennan and Shaver, *loc. cit.*
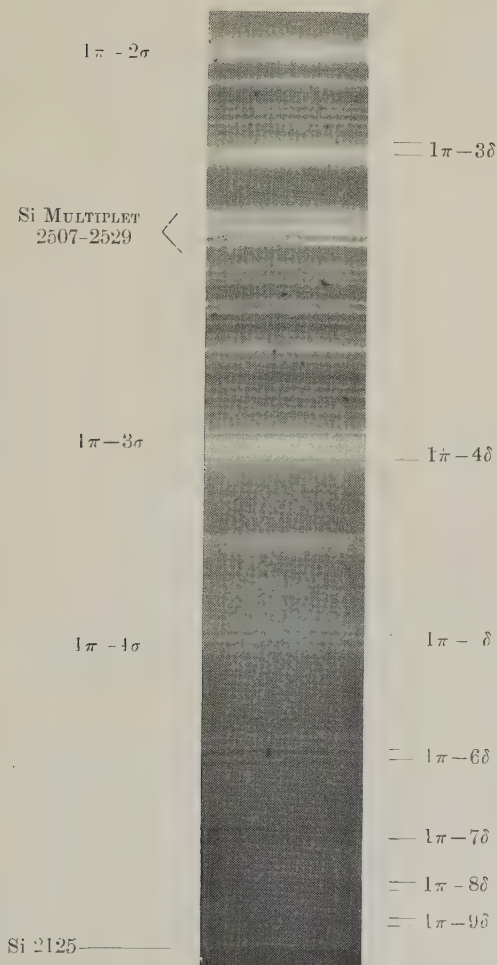
Under-water arc spectrum of aluminium-silicon alloy, showing
subordinate series of aluminium in absorption.

ALUMINIUM.

In this arc twelve absorptions appeared, in addition to those observed by L. and E. Bloch † in the under-water spark. Prominent among these was the remainder of the diffuse series.

Previous observers ‡ have identified nine doublets of the diffuse series and five of the sharp. These series showed in our absorption photographs to the eighth and fourth doublets respectively, although two lines of the sharp series were obscured by stronger lines of the diffuse series. The accompanying plate shows these absorptions.

The following table gives the series designations of the absorptions identified :—

$$\left.\begin{array}{l} *3961\cdot54 \\ *3944\cdot03 \end{array}\right\} \ 1\pi-1\sigma$$

$$\left.\begin{array}{l} *3092\cdot72 \\ *3082\cdot16 \end{array}\right\} \ 1\pi-2\delta$$

$$\left.\begin{array}{l} *2660\cdot39 \\ *2652\cdot48 \end{array}\right\} \ 1\pi-2\sigma$$

$$\left.\begin{array}{l} *2575\cdot11 \\ *2568\cdot00 \end{array}\right\} \ 1\pi-3\delta$$

$$\left.\begin{array}{l} 2378\cdot41 \\ 2372\cdot08 \end{array}\right\} \ 1\pi-3\sigma$$

$$\left.\begin{array}{l} *2373\cdot13 \\ *2367\cdot06 \end{array}\right\} \ 1\pi-4\delta$$

$$\left.\begin{array}{l} 2269\cdot09 \\ 2263\cdot45 \end{array}\right\} \ 1\pi-5\delta$$

$$\left.\begin{array}{l} 2263\cdot73 \text{ masked} \\ 2258\cdot00 \end{array}\right\} \ 1\pi-4\sigma$$

$$\left.\begin{array}{l} 2210\cdot05 \\ 2204\cdot63 \end{array}\right\} \ 1\pi-6\delta$$

$$\left.\begin{array}{l} 2174\cdot03 \\ 2168\cdot81 \end{array}\right\} \ 1\pi-7\delta$$

$$\left.\begin{array}{l} 2150\cdot59 \\ 2145\cdot39 \end{array}\right\} \ 1\pi-8\delta$$

$$\left.\begin{array}{l} 2134\cdot70 \\ 2129\cdot44 \end{array}\right\} \ 1\pi-9\delta$$

* Indicates absorptions noted by L. and E. Bloch.

† L. and E. Bloch, *loc. cit.*
‡ Grünter, *Zeit. f. wiss. Phot.* xiii. p. 1 (1914); Kayser and Runge, ' Handbuch der Spectroscopie.'

XC. *A Note on the Vibration of the* CO_3-*ion.*
By S. Chapman, *F.R.S., and* A. E. Ludlam, *M.Sc.*[*]

THE object of this note is to draw attention to a difficulty affecting the simple theory of the infra-red frequencies of vibration of the CO_3^{--}-ion given recently in a valuable paper by H. Kornfeld [†]. The theory is based on the simplified hypotheses (i.) that the ion behaves as if it were isolated and unaffected by neighbouring ions or molecules, and (ii.) that it is composed of three O^{--} ions situated at the corners of an equilateral triangle with a C^{++++}-ion at the centre. The observed infra-red frequencies are $w_1 = 1\cdot63 . 10^{14}$ sec.$^{-1}$, $w_2 = 2\cdot88 . 10^{14}$ sec.$^{-1}$, $w_3 = 1\cdot29 . 10^{14}$ sec.$^{-1}$; the first one being polarized in the plane of the ion, and the other two perpendicularly to this plane. Brester [‡] had already indicated that a triangular system of this type should possess three optically active oscillations, the motion being perpendicular to the plane in one case, and in the plane in the other two cases.

Kornfeld's treatment of the problem was not intended to be more than approximate, and was successful in leading to results of the right order of magnitude. In some respects, however, they are in definite disagreement with observation, and it is of interest to examine whether the theory can be modified to give a closer fit.

In Kornfeld's theory complete ionization of the C and O ions was assumed, but this admittedly rough approximation to the probable facts was improved by taking into account the polarization of the O ions by each other and by the C ion : a coefficient of polarization, α, was assumed for the O ions, such that the moment produced by an electric field E was α E. In calculating E the electrostatic charges $-2e$ and $4e$ of the O and C ions were alone considered : the secondary fields of the doublets themselves were ignored. In addition it was assumed that a repulsive force of potential $be^2 R^{-5}$ exists between the C and O ions, R being their mutual distance.

Kornfeld attempted to determine α, b, and the equilibrium value of R $(=r)$ from the condition of equilibrium of the ion and from the observed values of the frequencies. Having four conditions to satisfy by means of only three

* Communicated by the Authors.
† H. Kornfeld, *Zeitschr. f. Phys.* xxvi. p. 205 (1924).
‡ C. J. Brester, *Zeitschr. f. Phys.* xxiv. p. 324 (1924).

disposable constants, a perfect fit was impossible, and a least-squares solution was adopted which was moderately satisfactory and led to the values

$$r = 1\cdot 52 \cdot 10^{-8}\,\text{cm.}, \quad \alpha = 0\cdot 88 \cdot 10^{-24}\,\text{cm.}^3$$

(The determined value of b was not given.)

The latest determinations of r give $1\cdot 25$ Å., and the difference between this and $1\cdot 52$ Å. seems definitely outside the range of experimental error; it would, moreover, produce large discrepancies in the corresponding calculated values of the frequencies. The value of α is also not in good accord with the value determined from molecular refraction, viz. $3 \cdot 10^{-24}$ cm.^{3}, but the difficulty of reconciliation is perhaps less in this case.

In reviewing the possibilities of improving this numerical theory, it seemed to us convenient to take r and, possibly, also α, as well as w_1, w_2, and w_3, as experimentally known, and to use them to determine the repulsive forces between C and O ions and also between the O ions themselves. The latter forces were not considered at all by Kornfeld; but while a repulsive force between the C and O ions is obviously necessary for the stability of the CO_3 group, it seemed to us not unlikely that the O ions may be kept apart rather by repulsions between themselves than by the repulsion from the C-ion. We expressed the potential of these forces as $ae^2 R^{-n}$ between the C and O ions, and $ce^2 R^{-m}$ between the O ions, and sought to determine a, c, n, and m. The calculations indicated that m and n were each about 6, but this result was rendered of little interest owing to the fact that the values determined for a and c were of opposite sign, implying that the additional force between the O atoms must be attractive and not repulsive.

This improbable conclusion led to a re-examination of the equations, which were merely slight generalizations of those given by Kornfeld. From this it appeared that the contradiction between the data and the theory (in either form) is very simple and definite, as the following will indicate.

The equilibrium condition (*cf.* equations 7 and 26 *a* of Kornfeld's paper) is

$$8 - \frac{na}{r^{n-1}} + \frac{8\alpha}{r^3}(4 - \sqrt{3}) - \frac{4}{\sqrt{3}} - \frac{3mc}{(\sqrt{3})^{m+2}r^{m-1}} + \frac{2}{3}\cdot\frac{\alpha}{r^3}(4 - 4\sqrt{3}) = 0, \quad . \quad . \quad . \quad (1)$$

which gives one relation between a/r^{n-1}, c/r^{m-1}, and α. The

value of w_1 is given by the equations (*cf.* equations 18, 19, and 26 a of Kornfeld's paper)

$$w_1{}^2 = \frac{15}{4} \cdot \frac{e^2}{r^3} \cdot \frac{1}{m_0} \left\{ 8 - \frac{na}{r^{n-1}} + \frac{8\alpha}{r^3}(4 - \sqrt{3} \right\}, \quad . \quad (2)$$

(where m_0 is the mass of the C-ion) which gives a second relation between a/r^n and α.

Inserting the observed values, $r = 1.25$ Å., and $w_1 = 1.63$ 10^{14} sec.$^{-1}$, in these equations and transforming them so as to connect a, n, and α, and c, m, and α, respectively, we find

$$na = (1.25 \cdot 10^{-8})^{n-1} \{ 9.290 \, \alpha \, 10^{24} + 6.797 \}$$

and

$$mc = -\sqrt{3}(\sqrt{3} \cdot 1.25 \cdot 10^{-8})^{m-1} \{ .9995 \, \alpha \, 10^{24} + 1.080 \}.$$

The coefficient of polarization, α, is necessarily positive : the most favourable case, when $\alpha = 0$, still gives a negative value for c (implying an attraction between the O ions) ; in order to obtain a positive value of c in this case, it is necessary to increase the value of r in equations (1) and (2) to at least 1.4 Å.

One source of error in the theory arises from the treatment of the ions as point masses, charges, and doublets ; in actual fact the polarization of the ions consists in a displacement of the O-nuclei from the centres of the electronic shells. The X-ray measurement of the position of the ion probably refers to the nucleus, where also the mass is concentrated ; the repulsive forces, on the other hand, are probably directed from the centres of the electronic shells. The distance between these two points is about 0.2 Å. or 0.3 Å. If this were taken into account in the above equations, the magnitude of na/r^{n-1} and mc/r^{m-1} would be altered slightly, but without affecting their signs. The difficulty consequently still remains.

It does not seem likely that any further slight modifications, or improved approximations, in the simple theory would suffice to remove this difficulty. It appears to us that the latter probably arises from the neglect to take account of the ions surrounding the CO_3-ion in the crystal on which measurements have been made. It is hoped to undertake an examination of the somewhat complicated effect of these neighbouring ions.

Imperial College,
    South Kensington,
        May 1925.

XCI. *On the Attachment of Electrons to Gas Molecules.*
By V. A. BAILEY, *M.A., D.Phil., Oxford, Associate*
Professor of Physics, University of Sydney *.

1. IT is well known that in some gases like oxygen,
nitric oxide, and moist gases generally the electrons
moving under a small electric force tend to form ions by
adhering to molecules at some of the collisions with the
latter.

In a uniform electric field Z and in a gas at pressure p,
the electrons will have a velocity of agitation u and a velocity
of drift W which are functions of (Z/p) only. Whatever
may be the mechanism by which an electron attaches itself
to a given kind of gas molecule, it is plain that in a large
number N of collisions between electrons and the gas
molecules a number hN will result in attachment to form
negative ions, where h is a definite number depending only
on the nature of the gas and on the velocity at collision u.

The variation of h with u in a given gas is a subject for
experiment, and nothing is at present known about h except
that it tends to vanish as u increases. Some physicists have
assumed that h is constant for a given gas, an hypothesis
which has nothing to justify it, and which is certainly
contradicted by Townsend's experiments on the determina-
tion of Ne in slightly moist gases, as well as by the more
recent experiments on the motion of electrons in oxygen.

In recent years the problem of determining h experi-
mentally has been attacked by L. B. Loeb, and his results
for several gases have been published in a number of papers
in the Physical Review and the Philosophical Magazine.
His calculated values of h depend mainly on the following
three factors :—

1. The hypothesis that h is independent of u.
2. The interpretation of certain experimental current-
   potential curves with "asymptotic feet."
3. The determination of electron "mobilities" by means
   of Rutherford's sinusoidal alternating field method.

The first factor is not definitely established by his experi-
ments, and thus weakens the value of his results; the
second factor involves some very doubtful methods; and the
third is a definitely erroneous experimental method. It
thus appears that Loeb's conclusions are not very reliable.

2. From several points of view, the determination of the

* Communicated by Prof. J. S. Townsend, F.R.S.

values of the probability of attachment h for different gases and different velocities of collision u is a matter of interest ; so a method of investigation has been developed which depends upon the following theory :—

A group of n electrons all moving a small distance dz in a gas at pressure p and under a uniform electric force Z will make $nu \cdot dz / Wl$ collisions with gas molecules, where W is the velocity in the direction of the electric force, u is the velocity of agitation, and l is the mean free path of an electron. Of these total collisions, $h(nu \cdot dz / Wl)$ will result in attachment to form as many ions, and so the n electrons form $\alpha n dz$ ions, where $\alpha = hu / lW$. It easily follows that the number of electrons arriving on a plane distant z from their starting plane is $n = n_0 \epsilon^{-\alpha z}$, where n_0 is their number initially. The remaining $n_0(1 - \epsilon^{-\alpha z})$ form ions which also arrive at the plane z.

In certain cases it may happen that the electrons become detached from the ions after a certain number of collisions with molecules ; while in other cases the electrons may never become detached. These two possible types are conveniently named temporary ions and permanent ions respectively. In this investigation the case where permanent ions occur will alone be considered.

Fig. 1.
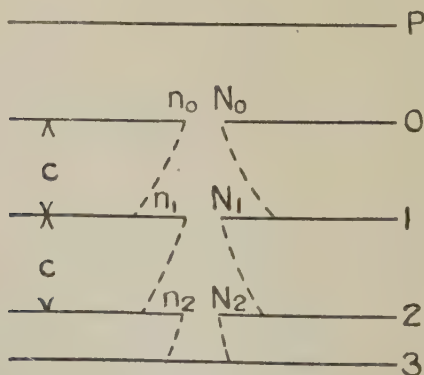
The principle of the apparatus used is illustrated by the diagram in fig. 1.

P, O, 1, 2, 3, are five parallel plates maintained at the potentials required to produce a uniform field throughout. Plates O and 2 are equidistant from 1, and all three have identical openings at the centre of each, of any convenient shape (*e.g.* a long narrow slit or a circle).

By means of ultra-violet light the plate P emits electrons which travel downwards under the influence of the field towards plate O. The stream which enters at the opening in plate O, consisting of both electrons and ions, diverges, so that only part of it passes through the opening in plate 1. This process is repeated in the space between plates 1 and 3.

Except for extremely small values of the electric force, the diffusion of the electrons in the stream is much larger than the diffusion of the ions, and consequently the stream becomes richer in ions as it passes each successive opening. This effect is intensified, of course, by the continual attachment of electrons to molecules. Let ξ denote the ratio of the currents received by electrodes 2 and 1 respectively, and η the ratio of the currents received by electrodes 3 and 2 respectively ; the ratios ξ and η for given values of Z and p are determined experimentally, and so the distribution ratio S may be calculated for each plate, S being the ratio of the current passing through an opening to the total current arriving on the plane containing that opening. Thus

$$S_1 = \frac{\xi(1+\eta)}{1+\xi(1+\eta)} \quad \text{and} \quad S_2 = \frac{\eta}{1+\eta}. \quad . \quad . \quad (1)$$

In unit time let n_0 electrons and N_0 ions pass through the opening in plate O, n_1 electrons and N_1 ions through the opening in plate 1, etc. Of the n_0 electrons, $n_0 \epsilon^{-ac}$ arrive as electrons on the plane 1 with a distribution ratio R_e, which is a known function $\phi^*(\lambda_e)$ of the variable $\lambda_e = NeZ/2k\Pi$, where N is the number of molecules per c.c. of a gas at 760 mm. pressure and 15° C., e the elementary charge, Z the electric force, k the factor by which the mean energy of agitation of the electrons exceeds that of an equal number of molecules of a gas at 15° C., and Π the normal atmospheric pressure of 760 mm.

Hence $\qquad n_1 = an_0, \quad \text{where} \quad a = R_e \epsilon^{-ac}.$

Similarly $\qquad n_2 = an_1 = a^2 n_0.$

The remaining $n_0(1 - \epsilon^{-ac})$ electrons go to form as many ions, which arrive on the plane 1 with a certain unknown distribution ratio r, and since the N_0 ions arrive at the same plane with the known distribution ratio $R = \phi(\lambda)$, where $\lambda = NeZ/2\Pi$, it follows that

$$N_1 = RN_0 + r(1 - \epsilon^{-ac})n_0,$$

or briefly $\qquad N_1 = RN_0 + bn_0.$

Similarly $\qquad N_2 = RN_1 + bn_1 = R^2 N_0 + (Rb + ba)n_0.$

* The method of determining ϕ is given in section 4.

3 H 2

On substituting the above values for n_1, n_2, N_1, and N_2 in the expressions

$$S_1 = \frac{n_1 + N_1}{n_0 + N_0}, \quad S_1 S_2 = \frac{n_2 + N_2}{n_0 + N_0},$$

one finds that $S_1 = (a + b - R) \cdot F + R,$

$$S_1 S_2 = (a + b - R) \cdot F \cdot (a + R) + R^2,$$

where $F = n_0/(n_0 + N_0),$

$$\therefore \quad S_1 S_2 - R^2 = (S_1 - R)(a + R).$$

and so $$a = \frac{S_1(R - S_2)}{R - S_1}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

It should be noticed that the possible occurrence of ions formed by clusters of molecules does not affect the above reasoning, for the distribution ratio for ions is independent of their masses.

From the experimental values of ξ and η the quantities S_1 and S_2 may be calculated by means of the relations (1), and consequently the value of a is also determined numerically.

The equation in two unknown variables $(\lambda_e$ and $\alpha)$, namely $\phi(\lambda_e)\epsilon^{-ac} = a$, requires to be supplemented by another relation between the two variables before either can be determined. In the case of an apparatus of fixed dimensions the supplementary equation is most conveniently obtained by utilizing the fact that if Z and p are altered respectively to Z/n and p/n, then λ_e and α are altered respectively to λ_e/n and α/n. In this way the simultaneous equations

$$\left. \begin{array}{l} \phi(\lambda_e)\epsilon^{-ac} = a_1 \\ \phi(\lambda_e/n)\epsilon^{-ac/n} = a_n \end{array} \right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

are obtained, with a_1 and a_n given experimentally, and so λ_e and α may each be determined *. The practical procedure is given in section 5.

3. The apparatus cntainoing the electrodes and the gas is represented in fig. 2, being constructed on principles similar to those employed in the instruments used for the determination of k and W in argon and hydrogen †, where the

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* If c could be varied, a second equation would be obtained without altering the pressure, thus providing an alternative method.

† J. S. Townsend and V. A. Bailey, Phil. Mag. xliv. Nov. 1922.

effect of impurities emanating from the apparatus was reduced to vanishing point.

The guard-rings R_0, R_1, R_2, R_3 and R_4, and the electrode

Fig. 2.
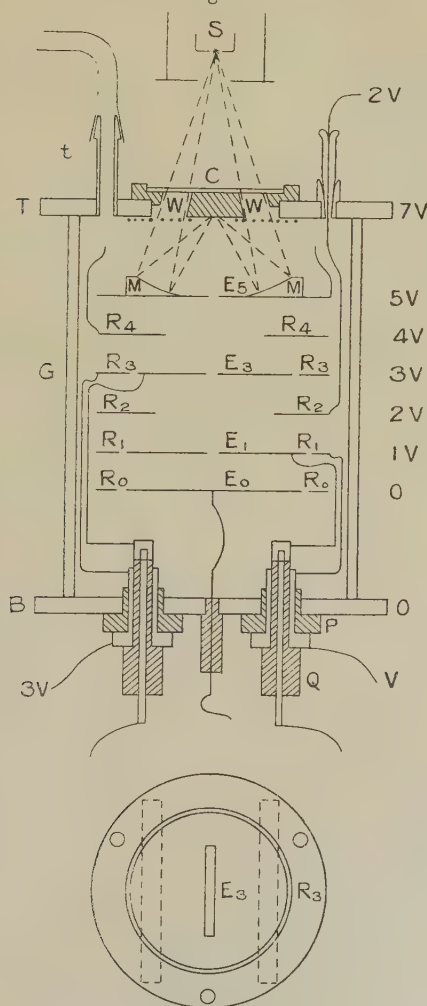
E_5 are mounted on three equidistant pillars which stand on the brass base B, the rings and electrode being insulated and fixed in position by means of distance pieces made of glass tubing. Each of the electrodes E_0, E_1, and E_3 is supported by two strips of plate-glass fixed to its own guard-ring. All

the rings and electrodes are silver plated in order to reduce the errors due to contact potentials. The glass cylinder G is cemented to B, and also to the brass top T which it supports. On T are mounted the glass capillaries, through which pass the connecting wires of R_2, R_4, and E_5, and the tube t, through which the gas is introduced or withdrawn. In the centre of T is a circular opening, into which fits the cover C which contains an annular quartz window W. On the electrode E_5 is mounted the silvered-brass ring M, whose polished upper surface is shaped as an annular part of a spherical mirror.

A uniform electric field is produced by maintaining the rings and electrodes at potentials proportional to their distances from the plane of R_0 and E_0, as indicated by the quantities 0, 1V, 2V . . . . 7V in fig. 2.

Part of the light from a spark-gap S (between aluminium electrodes) passes through the quartz window W and is reflected by the mirror M on to the central part of the under surface of the cover C ; this surface is of zinc, and so acts as a source of electrons. One advantage of this arrangement is that the cover C can be replaced, when desired, by another provided with a platinum wire which can be made incandescent, and so provides an alternative source of electrons.

The connecting wires from the electrodes E_0, E_1, E_3, and the rings R_1, R_3 are taken out through ebonite plugs in the base B of the instrument, but the inside exposed surfaces of the ebonite are kept very small, and as there is nothing but glass and metal elsewhere inside, the rate of contamination of the gas is very small.

Since the electrodes E_1 and E_3 are at a potential different from that of B (which is earthed), the principle of " split insulation " is adopted for their ebonite plugs in order to prevent electrical leakage over the surfaces which insulate their connecting wires. The ebonite plug P supports the brass plug which is shown connected to R_3 and maintained at the potential 3V by a connecting wire on the outside. This supports the ebonite plug Q, through which passes a brass rod connected to E_3. When an observation is being made, E_3 is insulated, but its potential is maintained practically constant at 3 V by electrical induction, and in consequence the leakage across the glass and ebonite insulators is quite inappreciable.

The electrodes E_5, E_3. and E_1 consist of outer rings fitted with inner rings over which silver foil is tightly stretched ; the openings in them consist of rectangular slits each 4 mm.

wide, all parallel to each other, and respectively 1·4, 4·7, and 6·5 cm. long. This type of opening was adopted mainly because it provides the case in which the ratio R is most easily computed. As the slit in E_5 is so much shorter than the other two, the calculation of R is identical with that for the case of infinitely long slits, and will be so considered in section 4.

Since the diameters of E_3, E_1, and E_0 are respectively 8, 9, and 9 cm., practically none of the electrons reach their boundaries, and consequently they may be treated mathematically as being infinitely large.

The distance between successive rings is 2 cm., and between successive slits 4 cm. ; the lower surface of T is 4 cm. above E_5.

In order to measure the ratios to each other of the currents to the electrodes E_3, E_1, and E_0, an elaboration of Townsend's induction-balance method was employed, which is illustrated by fig. 3. Each of the double-condensers C_1 and C_2 con-

Fig. 3.
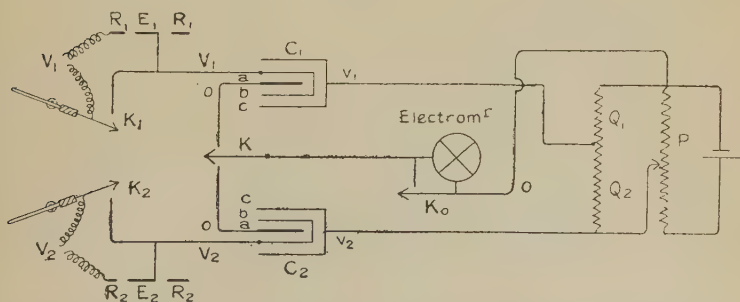
sists essentially of three concentric brass cylinders a, b, and c, all rigidly fixed and insulated from one another by means of ebonite rings. The method of split insulation is employed with a and b, so that no leakage from them across the insulating rings can occur. The electrode E_1 is connected to the cylinder b_1, and by means of the key K_1 may be brought to the potential V_1 of its guard ring R_1 and left insulated at that potential. Similarly E_2 is connected to b_2 and may be left insulated at V_2. The cylinders a_1 and a_2 may be connected in turn to an electrometer by means of the key K, and all three brought to zero potential with the earthing key K_0. By means of the resistance boxes Q_1 and Q_2 and the sliding potentiometer P, the outer cylinders c_1 and c_2 of the double-condensers may be brought to any desired potentials v_1 and v_2. Initially let a_1, a_2, and the

electrometer be insulated at zero potential, let the electrodes E_1 and E_2 with their attached cylinders be insulated at potentials V_1 and V_2 respectively, and let $v_1 = 0 = v_2$. When charges q_1 and q_2 arrive respectively on E_1 and E_2, the potentiometer and resistances can be adjusted so as to restore the potentials of all the insulated systems to their original values, provided the cylinders c are well screened from the cylinders a.

From the initial and final conditions of the system attached to E_1 we obtain the equation :—

$$q_1 = v_1 C_{1bc}.$$

Similarly $$q_2 = v_2 C_{2bc}.$$

If the condensers are made identical, then

$$C_{1bc} = C_{2bc},$$

and therefore $$q_1/q_2 = v_1/v_2 = Q_1/(Q_1 + Q_2).$$

In this way the ratios ξ and η may be determined experimentally.

The capacity coefficients C_{1bc} and C_{2bc} were compared by means of the arrangement illustrated in fig. 4.

<div align="center">Fig. 4.</div>
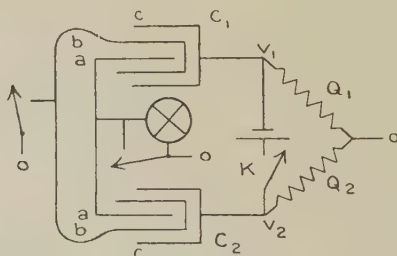
With the key K up the two systems a and b are earthed and then left insulated. For a certain value of the ratio Q_1/Q_2 the electrometer is unaffected by closing K. This corresponds to the equations

$$q_a = C_{aa}v_a + C_{ab}v_b,$$
$$q_b = C_{ba}v_a + C_{bb}v_b + C_{1bc}v_1 + C_{2bc}v_2,$$

with q_a, q_b, and v_a equal to zero initially and finally, and v_1, v_2, and v_b equal to zero initially.

The first equation shows that v_b will be zero finally, so the second equation reduces to

$$C_{1bc}v_1 + C_{2bc}v_2 = 0,$$

whence $$Q_1 C_{1bc} = Q_2 C_{2bc}.$$

The observations showed that the two coefficients were equal to within 1 per cent.

4. If the density of the electrons is assumed to be uniform across the first slit, then, for the apparatus described in the last section, the distribution ratio R is given by

$$R = \frac{\int_{-a}^{a} d\xi \int_{-a-\xi}^{a-\xi} q \, dx}{\int_{-a}^{a} d\xi \int_{-\infty}^{\infty} q \, dx},$$

Where *

$q = A c^{-\frac{1}{2}} \epsilon^{-\lambda x^2/2c}$,

ξ is the abscissa of a point in the plane of the first slit,

$2a$ is the width of a slit, namely 0·4 cm.,

c is the distance between successive slits, namely 4 cm.,

and $\lambda = NeZ/2\Pi k$, $= 20\cdot5 Z/k$ when Z is in volts/cm.

On putting $\lambda/2c = \theta^2$ and evaluating the denominator, this expression simplifies to

$$R = \frac{\theta}{2\sqrt{\pi}a} \int_{-a}^{a} d\xi \int_{-a-\xi}^{a-\xi} \epsilon^{-\theta^2 x^2} dx,$$

which may be further reduced to the convenient form

$$R = \text{erf}(v) - (1 - \epsilon^{-v^2})/v\sqrt{\pi}, \quad . \quad . \quad . \quad (4)$$

where $\quad v = 2a\theta = \sqrt{2\lambda a^2/c}$

and $\quad \text{erf}(v) = \frac{2}{\sqrt{\pi}} \int_{0}^{v} \epsilon^{-v^2} dv.$

The calculated values of R corresponding to different values of Z/k are given in Table I.

TABLE I.

Z/k.	R.	Z/k.	R.
·220	·167	6·25	·651
·390	·220	7·90	·688
·610	·271	9·75	·718
·878	·320	11·8	·744
1·56	·409	14·05	·765
2·44	·486	19·1	·798
3·52	·552	25·0	·824
4·78	·606		

* *Cf.* J. S. Townsend's ' Electricity in Gases,' p. 178.

Under actual experimental conditions the values of R will differ slightly from those in the above table for two principal reasons—namely, because the distribution of density of the electrons or ions across a slit is not quite uniform as assumed in the above calculation, and also because with widely-diverging streams there is a notable fraction of the electrons passing through a slit which diffuses to the edges of the latter.

If the electrons (or ions) originate in a line-source, it is easy to see that the density distribution across successive slits becomes less and less concentrated and asymptotically approaches a limiting condition which may be called the Permanent Distribution. Similarly, if the source is a slit of width $2a$ with uniform distribution of density, the Permanent Distribution is again asymptotically approached, but from the side opposite to that for the case of a line-source.

In order to determine this Permanent Distribution $q(x)$, it is necessary to solve an integral equation. But this problem may be avoided if it can be shown that the distributions $q =$ constant and $q = A\epsilon^{-\theta^2 x^2}$ at the first slit give nearly equal distributions at the second slit, for in that case either of the latter is a close approximation to the Permanent Distribution.

The two distributions at the second slit are most easily compared by evaluating the ratio $q(a)/q(o)$ for each of them.

For the first case :—

$$q(x) = B \int_{-a}^{a} \epsilon^{-\theta^2(x-y)^2} dy,$$

and so $[q(a)/q(o)]_1 = \mathrm{erf}\ (v)/2\ \mathrm{erf}\ (v/2)$.

Similarly in the second case :—

$$q(x) = A \int_{-a}^{a} \epsilon^{-\theta^2(x-y)^2 - \theta^2 y^2} dy,$$

so that

$$[q(a)/q(o)]_2 = \epsilon^{-v^2/8} [\mathrm{erf}\ (v/2\ \sqrt{2}) + \mathrm{erf}\ (3v/2\sqrt{2})]/2\ \mathrm{erf}\ (v)/\ \sqrt{2}.$$

The following figures provide a comparison of the distributions for the two cases, for different values of v :—

v.	$[q(a)/q(o)]_1$.	$[q(a)/q(o)]_2$.	R_1.	R_2.
·8	·866	·866	·409	·410
1·2	·754	·748	·552	·556
1·6	·658	·637	·651	·666
2·4	·550	·438	·765	·812

The last two columns give the corresponding values of the Distribution Ratio. For values of v up to 1·6 it is evident that the Permanent Distribution is closely approached at the second slit, and also that R_1 is a good approximation to the actual Distribution Ratio. For $v=2\cdot4$ the two distributions differ slightly, and the values of R_1 and R_2 differ by about 6 per cent.; the actual value of R will lie between these two, so that R_1 may be regarded as approximating to the actual Distribution Ratio to within about 3 per cent. for all values of R less than ·80.

It is not easy to calculate the effect of diffusion to the edges of the slit, so this was investigated by means of experiments which are described in the next section.

5. In order to examine these points and to test the accuracy of construction of the apparatus, experiments were made with pure hydrogen, for which gas the values of k are well established, and in which electrons remain free for a known range of values of Z/p *.

The hydrogen was generated by the electrolysis of a solution of barium hydrate and admitted into the apparatus through a hot palladium tube.

Some of the experimental results are shown in Table II., where p is the pressure of the gas in mm. of mercury, Z is the electric force in volts per cm., S_1 and S_2 are the observed distribution ratios for the electrodes 1 and 2 respectively (fig. 1), k is the energy factor determined in previous work on hydrogen, and R is the theoretical distribution ratio obtained from a curve representing the results in Table I.

TABLE II.

p.	Z.	S_1.	S_2.	Z/p.	k.	Z/k.	R.
2·14	10	·183	·193	4·7	25	·40	·22
4	10	·231	·248	2·5	17·1	·585	·265
4	20	·274	·292	5·0	26	·77	·300
8	5	·279	·294	·625	6·5	·77	·300
8	10	·295	·310	1·25	11·1	·90	·323
8	20	·338	·355	2·5	17·1	1·17	·361
16	5	·371	·385	·312	3·75	1·33	·382
16	10	·385	·402	·625	6·5	1·54	·405
16	20	·415	·435	1·25	11·1	1·80	·432
32	10	·476	·510	·312	3·75	2·67	·503
32	20	·510	·540	·625	6·5	3·08	·529

It will be noticed that when R is greater than ·36 its values are closely the same as those of S_2, but that S_2 is smaller than R and diverges more and more from it for values less than ·36. This behaviour is undoubtedly due to

* J. S. Townsend & V. A. Bailey, Phil. Mag. xlii. Dec. 1921.

the action of the edges of the slit on a widely divergent stream, and so S_2 may be taken to represent the correct distribution ratio for values of Z/k below 1·2. In the original experiments which determined the values of k for hydrogen, such an effect could not exist, as the distribution ratio was measured by means of three electrodes in the same plane, the middle one being a narrow strip separated from the others by ·5 mm. air-gaps. Consequently the values of k then obtained with widely divergent streams are quite reliable.

The values of S_1 are seen to be consistently about 6 per cent. less than those of S_2. If the instrument were constructed accurately and if the electrons always remained free, it might be expected that S_1 would be closely equal to S_2, especially for values less than ·55. The possibility that this discrepancy is due to the formation of ions, by electrons attaching themselves to hydrogen molecules, may be dismissed, for in that case the values of S_1 and S_2 for the same value of Z/p would converge to equality as p diminished, which evidently does not occur in Table II. Neither can the effect be attributed to the slit in E_1 being too short, for it is easy to show that more than 99 per cent. of the stream which would pass through an infinitely long slit does actually pass through the slit of length 6·5 cm., even when the divergence corresponds to $Z/k = 0·4$. From these and other considerations which need not be mentioned, it was concluded that the values of S_1 differed from those of S_2 partly because the uppermost field was not quite uniform, and partly because of slight errors in the dimensions and positions of the slits.

Consequently two distribution curves were required to be drawn for the instrument, one for each of the electrodes 1 and 2. For the latter the distribution ratio R'' was taken to be the same as the values of R given in Table I., which are greater than ·4 and the same as S_2 for larger divergencies. The values of R', the distribution ratio for electrode 1, were taken to be equal to ·94 S_1. The two curves shown in fig. 5 give R'' and R' in terms of Z/k.

It is now necessary to extend the theory given in section 2 to deal with the case of unequal distribution ratios. Let R', R_e', r' be the ratios for electrode 1, and R'', R_e'', r'' the ratios for electrode 2. If

$$a' = R_e' \epsilon^{-ac} \qquad b' = r'(1 - \epsilon^{-ac}),$$
$$a'' = R_e'' \epsilon^{-ac} \qquad b'' = r''(1 - \epsilon^{-ac}).$$

It is easily shown that

$$S_1 = (a' + b' - R') F + R',$$

$$S_1 S_2 = (a' + b' - R') F (R'' + \rho a') + R' R'',$$

where

$$\rho = \frac{a'' + b'' - R''}{a' + b' - R'};$$

$$\therefore \quad \rho a' = \frac{S_1 (R'' - S_2)}{R' - S_1}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Fig. 5.
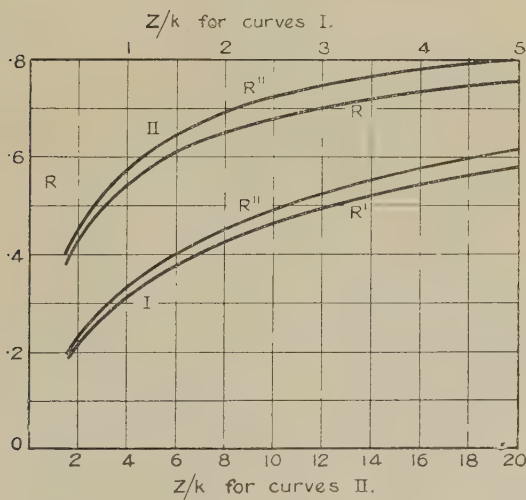
In order to determine the quantity ρ, it is necessary to calculate the quantity $b = r(1 - \epsilon^{-ac})$, which may be done in the following way. From the equations $q^* = A z^{-\frac{1}{2}} \epsilon^{-\lambda x^2/2z}$ and $\lambda_i = k \lambda_e$, it is evident that the distribution of the electrons at a plane distant z from the slit is the same as the distribution of ions which arrive from an identical slit situated at a distance kz above that plane. Of n_0 electrons passing through the actual slit, $n_0 \epsilon^{-\alpha z} \alpha . dz$ are converted into ions between the planes z and $z + dz$, which ions have the same distribution as the electrons, and consequently the distribution of ions which have arrived from an identical slit distant kz. When these newly-formed ions reach the

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* Or the equation $\dfrac{\partial^2 q}{\partial x^2} = 2\lambda \dfrac{\partial q}{\partial z}$.

electrode they will have travelled a further distance of $c - x$, and so possess a distribution ratio $R(v)$, where

$$v\sqrt{2\lambda_i a^2/(c + k - 1 . z)},$$

$R(v)$ being given by equation (4). Hence the number of ions formed in the distance c which pass through the second slit is

$$\int_0^c n_0 \alpha \epsilon^{-\alpha z} R\left(\sqrt{\frac{2\lambda_i a^2}{c + k - 1 . z}}\right) dz.$$

But this is the same as $b n_0$.

$$\therefore \quad b = \int_0^c \alpha \epsilon^{-\alpha z} R\left(\sqrt{\frac{2\lambda_i a^2}{c + k - 1 . z}}\right) dz.$$

Since the experiments with hydrogen showed that R''/R' is constant over the whole range, it follows from the last equation that $b''/b' = R''/R'$; also $a''/a' = R''/R'$. Therefore $\rho = R''/R'$, and so equation (5) becomes

$$a'' = \frac{S_1(R'' - S_2)}{R' - S_1}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

In equations (3), writing $R(Z/k)$ in place of $\phi(\lambda_e)$ and taking logarithms, it is found that

$$*\log_{10} a_1 - n \log_{10} a_n = \log_{10} R(Z/k) - n \log_{10} R(Z/kn).$$

If for a given value of n the curve

$$x = Z/k,$$
$$y = \log_{10} R(Z/k) - n \log_{10} R(Z/kn)$$

is drawn, using for this purpose the curve R'' in fig. 5, it may be employed to determine k in the following way. With an electric force Z and a pressure p the quantities S_1 and S_2 are observed, and so the quantity a_1 ($= a''$ in equation (6), is obtained. Similarly the quantity a_n, corresponding to the force Z/n and the pressure p/n, may be determined. The point on the (x, y) curve whose ordinate is equal to $\log_{10} a_1 - n \log_{10} a_n$ will have as abscissa the value of Z/k, and so k is obtained.

Three curves of this type have been calculated for the values of n : $\sqrt{2}$, 2, $2\sqrt{2}$, and are shown in fig. 6.

6. Two litres of air, obtained in a large open part of the grounds of the University of Sydney, was allowed to dry over caustic potash for sixteen weeks before being used for

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* In what follows, a stands for a'' and R for R''.

the determination of k and α. The observations were made with air-pressures of 8, 11·3, 16, and 22·6 mm., and forces of 5, 7·07, 10, 14·1, and 20 volts/cm. With the pressure 22·6 and the force 7·07 a large fraction of the current was found

Fig. 6.
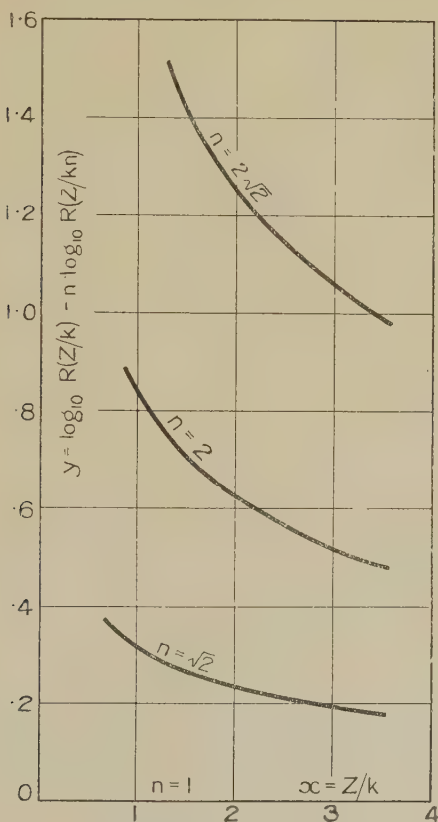
to be due to ions; and since under these conditions the error due to self-repulsion is of the same order as the experimental error, it was decided not to rely on measurements made with pressures higher than 22·6. The values of R'' and R' corresponding to the forces used were obtained from the curves shown in fig. 4, and are as follows :—

Z.	R''.	R'.
5	·615	·578
7·07	·671	·631
10	·720	·676
14·1	·765	·719
20	·802	·754

Examples of the observations made with air are shown in the following table, in which the quantity $-\log_{10}a$ is calculated with the aid of equation (6) and of the above values for R'' and R' :—

$p.$	$Z.$	$\xi.$	$\eta.$	$S_2.$	$S_1.$	$-\log_{10}a.$	$Z/p.$
22·6	10	·350	1·45	·592	·462	·559	·442
16	14·1	·305	·92	·480	·370	·520	·884
11·3	7·07	·250	·57	·363	·282	·604	·625
8	10	·210	·36	·265	·222	·653	1·25

The mean values of a large number of such measurements are given in the first four columns of Table III., being arranged in groups, each of which corresponds to a particular value of the ratio Z/p. The notation and units are the same as for Table II.

Table III.

$Z/p.$	$p.$	$Z.$	$-\log_{10}a.$	$k.$	$y.$	$\alpha.$	$(\alpha/p) \times 10^3.$
·312	22·6 16	7·07 5	·565 ·606	6·1	·565 ·606	·0645 ·0455	2·85
·442	22·6 16 11·3	10 7·07 5	·559 ·593 ·644	7·6	·559 ·593 ·644	·0765 ·0535 ·0380	3·36
·625	22·6 16 11·3 8	14·1 10 7·07 5	·511 ·546 ·605 ·680	9·9	·508 ·550 ·607 ·677	·0564 ·0391 ·0276 ·0190	2·44
·884	22·6 16 11·3 8	20 14·1 10 7·07	·482 ·521 ·579 ·673	13·7	·477 ·527 ·589 ·662	·0425 ·0299 ·0213 ·0150	1·88
1·25	16 11·3 8	20 14·1 10	·516 ·577 ·648	18·5	·516 ·576 ·648	·0282 ·0195 ·0138	1·73
1·77	11·3 8 5·65	20 14·1 10	·532 ·630 ·707	25	·540 ·619 ·714	·0057 ·0040 ·0023	·47
2·50	8 5·65	20 14·1	·602 ·690	32·5	·602 ·690	·0046 ·0029	·54

The method of determining the values of the energy factor k may be illustrated by the case of $Z/p = ·625$. In this group $Z = 14·1$ and Z/n is equal to 10, 7·07, 5 when n is equal to $\sqrt{2}$, 2, and $2\sqrt{2}$ respectively. The values of

$-n \log_{10} a_n$ are then respectively ·511, ·772, 1·210, 1·924. On the edge of a long strip of squared paper, points are marked representing these numbers to the same actual scale as that used for the ordinates in fig. 6. This strip is then placed on fig. 6 and moved, with its edge always parallel to the y-axis, until the marked points all simultaneously fall as nearly as possible on the curves corresponding respectively to $n=1$, $\sqrt{2}$, 2, and $2\sqrt{2}$. This occurs when the edge of the strip cuts the x-axis at the point given by $Z/k=1·42$, and so k is found to have the value 9·9.

In addition to determining k, this method provides to a certain extent an experimental test of the theory on which the experiments are based. In order to show this, the points on the edge of the strip where the curves cut it were noted, and the values of $-\log_{10} a_n$ were calculated from them by dividing by n. These values, which are given in the sixth column (under y) of Table III., show good agreement with the figures in the fourth column, and so it may be concluded that the experiments indicate that only *permanent* ions occur.

Fig. 7.
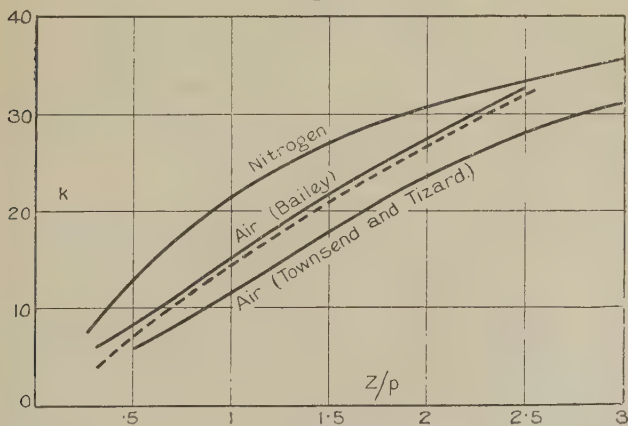
The values of k, shown in Table III., are represented by a curve in fig. 7, and may be compared with the curve for air which was obtained by Townsend and Tizard in 1913, and with the curve for nitrogen *.

The difference between the two curves for air may be partly explained by the fact that in the experiments of Townsend and Tizard no attempt appears to have been made to remove the carbon dioxide in the air used, which would

* J. S. Townsend & V. A. Bailey, Phil. Mag. xlii. Dec. 1921.

have a notable tendency to diminish the value of k in the range 5 to 30. If the flask in which the air was dried contained only phosphorus pentoxide, then the process of sealing off the top of the flask would tend to introduce a certain amount of carbon dioxide which would always remain in the gas. In the present experiments the caustic potash may be relied on to have removed the carbon dioxide completely.

In order to examine this point further, the values of k have been calculated from the values of S_1 obtained at the lowest pressures in each Z/p group and from the curve for R', which is the same method in principle as that used by Townsend and Tizard.

These are represented by the dotted curve, and as they give lower limits to the real values of k, it appears from the figure that the results obtained by Townsend and Tizard are somewhat lower than the true results for air which is dry and free from carbon dioxide.

The values of α have been calculated by means of the formula

$$\alpha_n = \cdot 575 [\log_{10} R(Z/kn) - \log_{10} a_n] *,$$

taking for the values of $-\log a_n$ the numbers given in the column under y in Table III.; these values of α and the mean values of $(\alpha/p) \times 10^3$ are given in the last two columns of the same table. The curve in fig. 8 represents $(\alpha/p) \times 10^3$ in terms of Z/p.

Fig. 8.
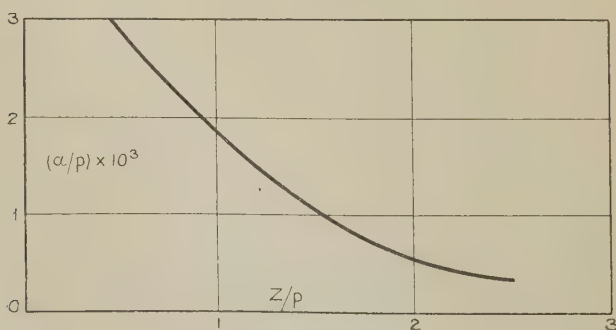
In Section 1 it was shown that $\alpha = hu/lW$, where h is the probability of attachment at a collision; on using the formula $W = \cdot 815 \ Zel/mu$ and the value $e/m = 1 \cdot 77 \times 10^7$ to

* Derived from the formula $a_n = R(Z/kn)\epsilon - a_n/c$.

eliminate l/u, it is found that

$$h = \frac{7\alpha W^2}{Z} \times 10^{-16}.$$

If the values for W obtained by Townsend and Tizard be adopted, the following values of h are obtained :—

Z/p.	·5.	1.	2.
h	$3\cdot3 \times 10^{-6}$	2×10^{-6}	$\cdot7 \times 10^{-6}$
u	$3\cdot3 \times 10^{-7}$	$4\cdot5 \times 10^{-7}$	6×10^{-7}

The values of the velocity of agitation u given in the last line are calculated for those of k obtained in the present experiments. It is clear from the way in which h varies with u that the view that h is a constant for a given gas is incorrect in the case of dry air.

If the lengths of the free paths of electrons in oxygen for the above values of u were known, it would be possible to deduce approximate values of h for that gas, since h is zero for nitrogen. For lack of such data nothing further can be stated than that h is probably of the order of 10^{-5} for oxygen. Experiments are now in progress with this gas, which, it is hoped, will give more direct information.

I feel much indebted to Prof. Townsend for a number of suggestions on the design of the apparatus used.

Note by Professor Townsend.

Prof. Bailey's method of investigating the motion of a stream of electrons affords a means of determining the rate at which ions are formed as the stream moves through a gas.

From the previous experiments on the motion of electrons, it is not possible to make a reliable estimate of the rate of formation of ions, but it was observed that certain impurities such as water-vapour may have a large effect in increasing the number of ions in the stream. An investigation of the motion of electrons in oxygen has just recently been made by Mr. Brose, which shows that in this gas the formation of ions may be due to impurities. He finds that oxygen becomes contaminated by its action on ebonite or elastic cements, which were used in the instruments with which the earlier measurements of the velocities were made, and that the number of ions formed in this gas is greatly reduced when the apparatus is constructed of materials on which oxygen has no chemical action and the surfaces are carefully cleaned.

XCII. *The Collapse of Short Thin Tubes by External Pressure.* *By* Professor G. COOK, *D.Sc., King's College, London* *.

A N historical survey † of the investigations which have been carried out in the subject of the collapse of tubes by external pressure reveals the very small part which elastic theory has played in the framing of formulæ and rules for practical design. The majority of experimenters in this field have been content to devise empirical formulæ to represent the results of their tests, a procedure which was, however, inevitable in the absence of an adequate theory. The important practical applications demanded some means of calculating the strength, and, as in many other engineering problems, practice could not wait for theory. The first theoretical solution was given by Bryan ‡ thirty years after Fairbairn § had carried out the tests upon which were based not only his own, but many other empirical formulæ which served for the purposes of design for upwards of fifty years.

It would not be claimed that any of the formulæ so obtained could legitimately be applied to cases which did not resemble very closely the conditions of the tests upon which they were based; but the existence of any mathematical theory appears to have been ignored for many years after Bryan had given his solution. Bryan's theory was incomplete in that it applied only to a long tube. Moreover, in the case of greatest practical importance, namely the cylindrical boiler furnace, other questions have to be considered in calculating the proportions. Nevertheless, it is not a little surprising that no attempt was made to test the theory until the experiments of Stewart ‖ and Carman ¶ were carried out in 1905. It was shown by these tests that the collapsing pressure was proportional to the cube of the ratio of the thickness to the diameter, as indicated by Bryan's formula, provided that the ratio was less than 0·025, but that there was a serious discrepancy between the numerical values, the formula giving results some 25 per cent. too great. The reason at first suggested for this difference ** was that the tubes tested were not perfectly circular nor of

* Communicated by the Author.

† A *résumé* and bibliography of the subject (up to 1913) was given by the author in the British Association Report, 1913, p. 213.

‡ Proc. Camb. Phil. Soc. vol. vi. (1888).

§ Phil. Trans. 1858.

‖ Trans. Amer. Soc. Mech. Eng. vol. xxvii. (1905–6).

¶ Univ. of Ill. Bulletin, No. 17 (1906).

** Slocum, ' Engineering,' Jan. 8, 1909.

perfectly uniform thickness. It was later pointed out by Southwell * that a more likely explanation was to be found in the fact that for any but extremely thin tubes elastic breakdown would take place before the pressure given by Bryan's formula was reached, a conclusion which was supported by the fact that agreement with the formula was closest for the thinnest tubes.

While, therefore, with this qualification, it may be said that in the case of long tubes the theory is now adequately confirmed by experiment, provided that the conditions assumed by the theory are fulfilled, the position in regard to the short tube is much less satisfactory.

The first successful mathematical investigation of the collapsing pressure of a short tube was by Southwell †, who gave the general formula

$$p = 2\mathrm{E}\,\frac{t}{d}\left[\frac{\mathrm{C}}{k^4(k^2-1)}\,\frac{d^4}{l^4} + \frac{1}{3}\frac{m^2}{m^2-1}\cdot(k^2-1)\,\frac{t^2}{d^2}\right], \quad (1)$$

where p is the collapsing pressure, t the thickness, d the diameter, l the length, E Young's modulus, $\frac{1}{m}$ Poisson's ratio, k the number of lobes or waves into which the circumference divides at the moment of collapse, and C a constant depending on the type of the constraints at the ends of the tube. In the above expression the value of k to be taken is that whole number which, for given values of t, d and l, will make p a minimum.

Southwell's investigation gave the first complete explanation of the well-known manner in which a short tube collapses into a number of lobes which increases as the length of the tube diminishes. It also indicated the general manner in which the pressure would vary with the length. The difficulty arises in attempting to give a numerical solution.

As has been already stated, the constant C depends on the type of the end constraints. There are only two types which need be considered: namely (1) where the ends are constrained to remain circular and cylindrical, and (2) where they are constrained to remain circular, but are not clamped longitudinally. The first type is analogous to the fixed-ended strut, or the encastré beam, and is the type to be found in all practical cases. It is also the type which has been adopted, as far as the author can discover, in all experimental work.

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* Phil. Mag. Sept. 1913.
† Phil. Trans. (A) vol. ccxiii. (1913); Phil. Mag. May 1913.

Unfortunately, it is a type for which it has not, so far, been found possible to give a numerical value to the constant C; and for this case, therefore, Southwell's formula does not give a numerical result. Moreover, even if a solution were available, its verification for this type of end-constraint would be largely prevented by the difficulty of providing means for fixing the ends which did not introduce initial strains of an entirely unknown amount, but certainly comparable to those existing in the tube just prior to collapse.

On the other hand, for the second type of constraint, where the ends are kept circular without restricting the slope of the tube-wall, the constant C is determinate, and a slight extension of Southwell's analysis leads to the result

$$C = \frac{\pi^4}{16},$$

and for the collapsing pressure

$$p = 2E \frac{t}{d} \left[\frac{\pi^4}{16 k^4 (k^2 - 1)} \cdot \frac{d^4}{l^4} + \frac{1}{3} \frac{m^2}{m^2 - 1} \cdot (k^2 - 1) \frac{t^2}{d^2} \right]. \quad (2)$$

Southwell regarded this type of constraint as purely ideal. In so far as it is never found in practice, this description is just; but, on the other hand, by the method described below it can, for the purpose of experiment, be produced with greater simplicity, and with a very much closer approach to the ideal conditions, than can the fixed-ended type of constraint.

It appeared, therefore, to the author worth while to carry out some tests with this type of end-fixing, especially as, through the help of the Britannia Tube Company, of Birmingham, he was able to obtain some exceptionally thin brass tubing for the purpose. This tubing was 1·05 in. diameter, and by careful selection a number of specimens having an average thickness between 0·0083 and 0·0085 inch were obtained. The variation in thickness in any one specimen was not more than 5 per cent. from the mean, and in most cases was very much less than this. As received, the tubes were not round, but by placing them on an accurately fitting steel mandril, and rolling between surface plates, the irregularities were removed. While on the mandril, the tubes were cut to various lengths from 0·25 to 7 inches.

The manner in which the ends were closed in order to secure freedom from longitudinal constraint is shown in fig. 1. The end-pieces were machined with spherical surfaces in the region of contact with the tube. The tube was held between these surfaces by screwing gently on the central bar, which also acted as a strut to take the longitudinal compression when the external pressure was applied. Thin rubber bands placed round the lines of contact made perfectly

water-tight joints without producing any initial distortion. One end was also provided with a means of connecting the interior of the tube with the outside atmosphere. For the test, the tube was placed in a pressure vessel, pressures below 30 lb. sq. in. being read on a mercury column, and above that figure on a calibrated Bourdon pressure-gauge.

Fig. 1.
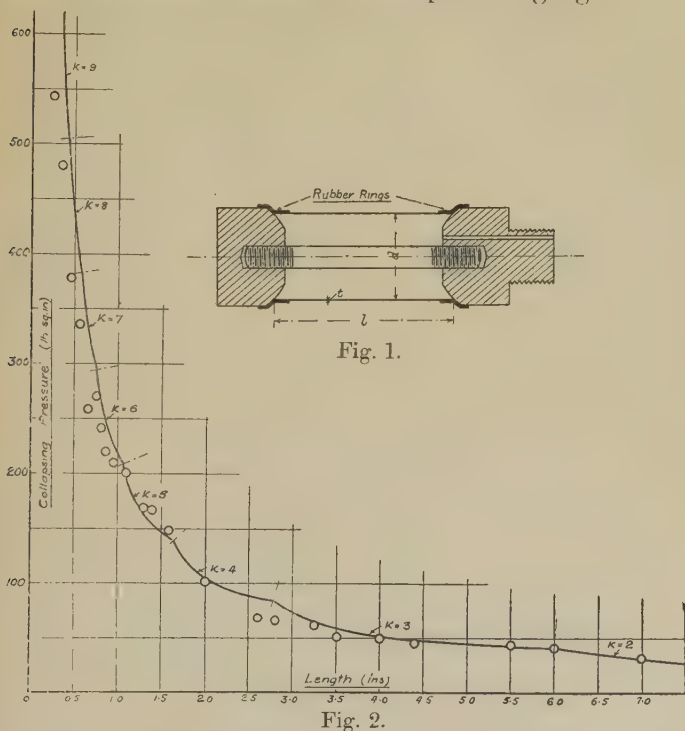
Fig. 2.

The results of the tests are given in the table and are plotted in fig. 2, together with the broken curve representing the formula (2). The value of Young's modulus was determined by the following method. Plugs were soldered into the ends of a tube, and to one end a connexion was made with a capillary tube of known diameter. The tube was filled with water and a known external pressure applied, the change in volume being measured by the displacement of the liquid in the capillary tube. The value of E thus obtained was $14 \cdot 0 \times 10^6$ lb. sq. in. Poisson's ratio has been taken as $0 \cdot 3$, a special determination being unnecessary in view of the fact that a large error in its value would affect the value of p, obtained by calculation, to a negligible extent.

The agreement between the calculated and observed

collapsing pressure is seen to be very satisfactory. It will be observed, however, from the table that the number of lobes in the collapsed tube does not correspond with that indicated by theory. It must be remembered that the final shape of the cross-section is not necessarily that which exists at the moment of collapse. The configuration calculated is that which, under the collapsing pressure, will be in a state of neutral equilibrium, and the actual displacements in this configuration are assumed to be consistent with perfect elasticity. In the final collapse this configuration will usually break down owing to the deformation proceeding more rapidly in one part than in another, and it would only be in rare cases that the initial configuration would be maintained in the unstable state immediately following the collapse. It is therefore to be expected that the observed number of lobes will usually be less than that predicted by theory, and this is actually seen to be the case. In most cases the collapse was fairly symmetrical, but in those cases for which no figure is given in the table the distortion was too irregular to describe the shape.

Results of Tests on Thin Brass Tubes.
Diameter 1·05 mm.

No.	Thickness *t* (in.).	Length *l* (in.).	Collapsing Pressure (lb. sq. in.).	No. of lobes in cross-section.	
				Observed.	Calculated.
1	0·0084	0·25	543	8	11
2	0·0084	0·35	480	6	9
3	0·0084	0·45	378	6	8
4	0·0084	0·54	336	5	7
5	0·0083	0·65	259	5	7
6	0·0085	0·75	270	5	6
7	0·0083	0·80	241	4	6
8	0·0083	0·84	218	...	6
9	0·0083	0·95	210	...	6
10	0·0084	1·10	201	...	5
11	0·0084	1·30	169	...	5
12	0·0084	1·40	167	...	5
13	0·0085	1·59	148	4	5
14	0·0084	2·00	101	3	4
15	0·0084	2·60	68	3	4
16	0·0085	2·80	65·5	3	3
17	0·0084	3·25	61	3	3
18	0·0084	3·50	51	3	3
19	0·0084	4·00	49	3	3
20	0·0083	4·40	46	2	3
21	0·0083	5·50	44	2	3
22	0·0085	6·00	40·5	2	2
23	0·0085	7·00	32·2	2	2

XCIII. *Ionic Equilibria across Semi-Permeable Membranes.* By NAOTO KAMEYAMA [*].

1. *Introduction.*

IN a paper published in 1914 (F. G. Donnan and A. J. Allmand, Trans. Chem. Soc. 105, p. 1941, 1914) an account was given of an investigation of the distribution of potassium chloride between two aqueous solutions separated by a membrane of copper ferrocyanide, one of the solutions containing potassium ferrocyanide in addition to potassium chloride. The theoretical treatment of the results was rendered unsatisfactory owing to the difficulty of determining ionic concentrations in mixed salt solutions, and to the divergence of the ions from "ideal" behaviour, whilst an electrometric test of the equilibria was complicated by the necessity of having to use potassium iodide instead of potassium chloride in the reversible galvanic cells. As pointed out in the paper referred to, the present state of the theory of electrolytic solutions renders it necessary to employ in the calculations activities and activity-coefficients. This procedure is applied in the present paper to the measurements of Donnan and Allmand and to a number of new measurements of the same equilibrium, *i. e.*

$$KCl + K_4Fe(CN)_6 \qquad \Big| \qquad KCl$$
$$(1) \qquad\qquad\qquad (2)$$
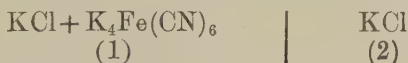
where the vertical line denotes the membrane of copper ferrocyanide gel. If we denote partial molar free energies by the symbol $\overline{F}$, the isothermal-isobaric condition of equilibrium requires the equation

$$(\overline{F}_K)_1 + (\overline{F}_{Cl})_1 = (\overline{F}_K)_2 + (\overline{F}_{Cl})_2$$

or, in terms of ionic activities,

$$[K]_1 . [Cl]_1 = [K]_2 . [Cl]_2,$$

where, for simplicity of writing, the symbol $[\ ]$ denotes not the concentration but the activity of the corresponding ion.

Writing $[K] = f_K m_K$, where the symbols f and m denote activity-coefficient and stoichiometric molarity respectively, the equation of equilibrium becomes

$$(f_K . f_{Cl})_1 . (m_K . m_{Cl})_1 = (f_K . f_{Cl})_2 . (m_K . m_{Cl})_2.$$

If, following the nomenclature of G. N. Lewis, we write

$$f = (f_K . f_{Cl})^{\frac{1}{2}}, \quad m = (m_K . m_{Cl})^{\frac{1}{2}},$$

where f and m now denote the mean (ionic) activity-coefficient

* Communicated by Prof. F. G. Donnan, F.R.S.

and the mean (ionic) molarity, the equation of equilibrium may be written in the brief form

$$f_1 m_1 = f_2 m_2.$$

In this equation m_1 and m_2 are known from the chemical analysis of the equilibrium solutions, whilst the value of f_2 (the mean activity coefficient for a pure aqueous solution of potassium chloride) can be obtained by interpolation from known data; hence the value of f_1, the mean activity-coefficient of potassium chloride in the solution containing also potassium ferrocyanide, can be calculated. According to the investigations of G. N. Lewis, the mean activity-coefficient of a salt such as KCl in a solution of mixed salts should, for solutions which are sufficiently dilute, depend only on the "ionic strength" (μ) of the solution, and this conclusion has been confirmed by the results of other investigators and by the recent theory of Debye and Hückel. The type of equilibrium discussed in the present paper affords, therefore, an opportunity of testing the validity of the "ionic strength principle" in the interesting case where an aqueous solution of potassium chloride contains another salt (potassium ferrocyanide) with a tetravalent anion. In this solution the ionic strength is given by the equation

$$\mu = \tfrac{1}{2}(m_K + m_{Cl} + 4^2 \cdot m_{e(CN)_6}) = m_{Cl} + 2\cdot 5\ n_{Fe(CN)_6},$$

because

$$m_K = m_{Cl} + 4 m_{Fe(CN)_6} = m_{Cl} + n_{Fe(CN)_6},$$

where the symbol n denotes the normality of the potassium ferrocyanide.

If the ionic strength principle holds strictly, the calculated value of f_1, obtained from the equation

$$f_1 = \frac{m_2}{m_1} f_2$$

should be equal to f_0, the activity-coefficient of potassium chloride in a pure aqueous solution of this salt of equal ionic strength. Thus the ratio f_1/f_0 measures the deviation (if any) from this principle in the solutions containing potassium chloride and potassium ferrocyanide, or, if we assume the principle to hold good, the same ratio will measure the deviation of the experimental results from those calculated on the basis of the principle.

In cases of ionic distribution equilibrium, such as one discussed in this paper, the system is not in complete equilibrium unless

$$(\overline{F}_{H_2O})_1 = (\overline{F}_{H_2O})_2,$$

and if the partial molar free energies of the water are not made equal by the addition to one solution of a non-permeating non-electrolyte (such as sucrose), then the water equilibrium requires a difference in the pressures (osmotic equilibrium). Since in the new measurements given in this paper, the osmotic (water) equilibrium as well as the ionic (salt) equilibrium was attained, it is necessary to consider whether these pressure differences will have any measurable effect on the calculated activity-coefficients.

Now

$$\overline{V}_K = \left(\frac{\partial \overline{F}_K}{\partial P}\right)_T = RT\left(\frac{\partial \log [K]}{\partial P}\right)_T = RT\left(\frac{\partial \log f_K}{\partial P}\right)_T,$$

and therefore

$$\frac{1}{f_K}\left(\frac{\partial f_K}{\partial P}\right)_T = \frac{\overline{V}_K}{RT};$$

similarly

$$\frac{1}{f_{Cl}}\left(\frac{\partial f_{Cl}}{\partial P}\right)_T = \frac{\overline{V}_{Cl}}{RT};$$

hence

$$\frac{1}{f_{KCl}}\left(\frac{\partial f_{KCl}}{\partial P}\right)_T = \frac{\overline{V}_K + V_{Cl}}{2RT} = \frac{V_{KCl}}{2RT},$$

where

$$f_{KCl} = (f_K \cdot f_{Cl})^{\frac{1}{2}}.$$

For a moderate pressure change ΔP we may therefore write with sufficient approximation

$$\frac{\Delta f_{KCl}}{f_{KCl}} = \frac{\overline{V}_{KC}}{2RT} \cdot \Delta P.$$

For aqueous solutions of potassium chloride at $25°$

m_{KCl}	0·1668	0·2740	0·3385	0·6840	0·9472
$\overline{V}_{KCl(c.c.)}$	+ 28·0	28·5	28·7	29·4	29·7

Taking the value $\overline{V}_{KCl} = 28·0$ we get

$$\frac{\Delta f_{KCl}}{f_{KCl}} = 6 \cdot 10^{-4} \Delta P,$$

where ΔP is measured in atmospheres. This equation gives an increase in f_{KCl} of $0·06$ per cent. per one atmosphere difference of pressure, an amount which is quite negligible in the present investigation.

2. *Recalculation and Discussion of the Results of Donnan and Allmand.*

The concentrations of the equilibrium solutions obtained in the experiments of Donnan and Allmand are shown in columns B to D of Table I., the concentrations being

TABLE I.

	A. Exp. No.	B. Solution 1 K₄Fe(CN)₆.	C. Solution 1 KCl.	D. Sol. 2 KCl.	E. $\frac{m_2}{m_1}$	F. f_2.	G. $\mu_1^{\frac{1}{2}}$	H. f_1.	L. f_0.	J. $\frac{f_1}{f_0}$
Series I. K₄Fe(CN)₆ ca. 0.01 N.	27	8·6	9·0	13·1	1·041	0·911	0·1747	0·948	0·871	1·088
	28	10·1	9·8	13·8	0·9881	0·909	0·1874	0·898	0·862	1·042
	26	10·0	18·7	22·5	0·9713	0·886	0·2091	0·860	0·849	1·014
	25	9·3	17·9	21·3	0·9651	0·888	0·2030	0·857	0·852	1·006
	24	9·1	44·9	48·7	0·9891	0·841	0·2602	0·832	0·820	1·014
	23	10·2	46·0	49·7	0·9775	0·840	0·2674	0·821	0·817	1·003
	22	10·6	94·1	96·9	0·9761	0·796	0·3473	0·777	0·782	0·994
	21	8·7	93·9	96·2	0·9800	0·797	0·3402	0·781	0·785	0·996
	19	9·4	227·7	227·8	0·9802	0·739	0·5012	0·724	0·734	0·987
	20	9·7	228·0	228·8	0·9826	0·739	0·5023	0·726	0·733	0·991
Series II. K₄Fe(CN)₆ ca. 0.02 N.	17	18·9	11·0	16·9	0·9317	0·900	0·2415	0·830	0·830	1·010
	18	18·5	11·2	17·8	0·9759	0·897	0·2398	0·875	0·831	1·053
	13	19·3	21·9	28·3	0·9421	0·873	0·2650	0·822	0·818	1·006
	14	18·8	23·1	28·8	0·9258	0·872	0·2647	0·807	0·818	0·997
	1–10	19·2	46·3	52·8	0·9588	0·837	0·3071	0·802	0·798	1·006
	15	19·7	115·3	121·0	0·9699	0·781	0·4053	0·758	0·762	0·994
	16	18·2	118·6	124·0	0·9731	0·780	0·4052	0·759	0·762	0·996
	11	19·3	220·1	223·4	0·9731	0·741	0·5181	0·721	0·728	0·991
	12	18·5	223·5	228·0	0·9802	0·739	0·5195	0·724	0·727	0·996

TABLE I. (*continued*).

	A.	B.	C.	D.	E.	F.	G.	H.	I.	J.
		Solution 1.		Sol. 2.						
	Exp. No.	$K_4Fe(CN)_6$	KCl.	KCl.	$\frac{m_2}{m_1}$	f_2.	$\mu_1^{\frac{1}{3}}$	f_1.	f_0.	$\frac{f_1}{f_0}$
Series III. $K_4Fe(CN)_6$ ca. 0·05 N.	29	46·7	8·4	20·1	0·9342	0·892	0·3538	0·833	0·779	1·070
	30	49·6	8·7	20·4	0·9057	0·891	0·3643	0·807	0·776	1·040
	31	46·8	16·1	28·8	0·9051	0·872	0·3649	0·789	0·776	1·017
	32	46·7	16·1	28·7	0·9026	0·872	0·3646	0·787	0·776	1·015
	33	48·8	43·3	57·6	0·9120	0·831	0·4066	0·758	0·762	0·995
	34	48·9	46·5	60·8	0·9124	0·828	0·4109	0·756	0·760	0·995
	35	48·3	89·2	102·6	0·9262	0·792	0·4582	0·734	0·746	0·983
	36	48·1	87·8	101·0	0·9245	0·793	0·4562	0·733	0·747	0·980
	37	49·0	226·3	238·8	0·9568	0·735	0·5906	0·703	0·708	0·993
	38	48·1	225·3	238·0	0·9590	0·736	0·5879	0·706	0·709	0·996
Series IV. $K_4Fe(CN)_6$ ca. 0·1 N.	39	96·1	5·1	25·2	1·109	0·880	0·4955	0·976	0·736	1·326
	40	94·6	8·2	26·4	0·9092	0·878	0·4946	0·798	0·736	1·085
	43	97·4	43·7	68·6	0·8736	0·820	0·5359	0·716	0·723	0·991
	44	96·1	43·2	68·4	0·8818	0·820	0·5371	0·723	0·722	1·002
	45	98·3	88·8	116·2	0·9018	0·784	0·5785	0·707	0·711	0·994
	46	100·8	92·1	116·3	0·8926	0·784	0·5866	0·684	0·709	0·965
	47	95·0	226·3	253·8	0·9412	0·731	0·6811	0·688	0·686	1·003
	48	97·3	221·0	251·3	0·9479	0·732	0·6814	0·694	0·686	1·011

expressed in milli-equivalents per litre. The ratio m_2/m_1 is given by $D/\sqrt{(B+C)C}$, where B, C, and D denote the concentrations given in the corresponding columns. The values of f_2 are obtained by interpolating at the requisite values of the ionic strength from the curve shown in fig. 1,

Fig. 1.
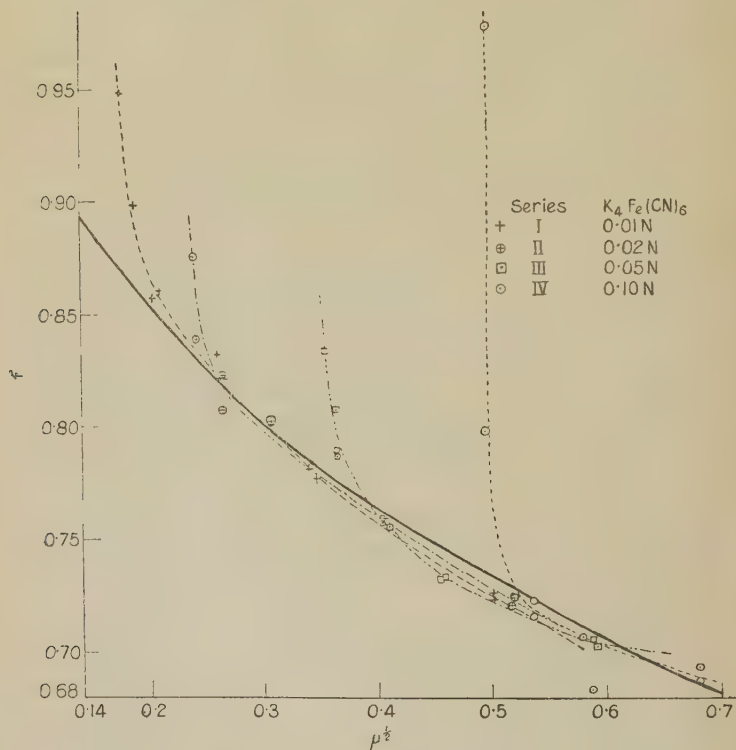
in which the mean activity-coefficient of potassium chloride in the pure aqueous solution at $25°$ is plotted against the square root of the ionic strength, using the following data :

m ...	0·005	0·01	0·02	0·05	0·1	0·2	0·5
$\mu^{\frac{1}{2}}$...	0·0707	0·1000	0·1415	0·2237	0·3162	0·4472	0·7071
f ...	0·946	0·922	0·892	0·840	0·794	0·749	0·682

The values of f_1 are calculated from the equation $f_1 = \dfrac{m_2}{m_1} f_1$, and are plotted against the corresponding values of $\mu^{\frac{1}{2}}$ in fig. 1, whilst the values of f_0, the activity-coefficient in a pure aqueous solution of potassium chloride of the same

ionic strength as the solution corresponding to f_1, are obtained by interpolation from the given potassium chloride activity curve.

In these calculations two points require notice. The concentrations as obtained from the analyses of the equilibrium solutions are expressed per litre, whilst in the activity-coefficient curve for potassium chloride the concentrations are expressed per kilogram of water in the solution. Owing to the dilution of the solutions, a simple calculation shows that the error thus introduced into the values for f_1 and $\mu_1^{\frac{1}{2}}$ will never exceed 0·5 per cent., and will usually be much smaller. Secondly, the experiments were carried out at room temperature, whilst the activity-coefficient curve holds for 25°. Since the difference of temperature is small and the calculations assume only that the temperature coefficient of the activity-coefficient of potassium chloride has the same value in a pure solution as in a solution containing also potassium ferrocyanide, no appreciable error can arise from this source.

An examination of the values of f_1/f_0 given in Table I. shows that in general there is a good approximation to unity. Only in eight cases throughout the whole series of experiments is the deviation from unity greater than 2 per cent. There appears, however, to be a more or less systematic deviation from unity ($f_1/f_0 > 1$) when the concentration of potassium chloride is comparable, or small in comparison, with that of potassium ferrocyanide (experiments 27, 28, 29, 30, 39, 40). If there be no systematic experimental error, this result would appear to indicate that the activity-coefficient (f_1) of a very dilute solution of potassium chloride in an aqueous solution of potassium ferrocyanide of equal or much greater concentration is greater than in a pure aqueous solution of potassium chloride of equal ionic strength. Such a result would mean that the presence of the tetravalent ion tends to increase the activity-coefficient of the chloride ion in a manner not accounted for by the principle of ionic strength. However, as the Table and the curves show, this effect becomes insignificant when the potassium chloride concentration rises, since then the calculated value of f_1 coincides practically with the value (f_0) given by the activity-coefficient curve for pure potassium chloride. If the indicated deviation from the ionic strength principle really exists in the present case, we may consider how far it might be accounted for by the theory of Debye and Hückel (cf. *Physikal. Zeitsch.* p. 115, 1925, equation 85 *a*). The

activity-coefficient [*] of Cl ion at $25°$ is given by the equation

$$\log_{10}(f_{Cl})_1 = -0.118 \sqrt{2\mu} \cdot [B_{Cl} + C_1],$$

where B_{Cl} is a function of the " size " of the Cl ion, μ of the ionic strength of the solution only, whilst C_1 depends on these factors and also on the " size " of the other ions present in the solution. Comparing the values of f_{Cl} in two solutions of equal ionic strength, we get

$$\log_{10} \frac{(f_{Cl})_1}{(f_{Cl})_0} = -0.118 \sqrt{2\mu} \cdot [C_1 - C_0].$$

Since the following relations hold

$$C = \frac{\mu_{Cl}}{\mu} D_{Cl} + \frac{\mu_K}{\mu} D_K + \frac{\mu_{Fe(CN)_6}}{\mu} D_{Fe(CN)_6},$$

$$\mu = \mu_{Cl} + \mu_K + \mu_{Fe(CN)_6},$$

and since D is a function of the ratio r, where $r = a \big/ \frac{1}{K}$, a being the " radius " of the ion and $\frac{1}{K}$ that of the " ion-atmosphere " (which is determined by μ), it is clear that, as D decreases with increasing r and becomes zero in the limiting case, f_{Cl} will be larger in a solution ¦containing $K_4Fe(CN)_6$ than in a pure solution of KCl of equal ionic strength, provided that the ion $Fe(CN)_6$ is larger in dimensions than in the ion Cl. Referring $(f_{Cl})_0$ to a pure KCl solution, we can deduce the equation

$$C_1 - C_0 = -(1-x)(D_{KCl} - D_{K_4Fe(CN)_6}),$$

where D_{KCl} and $D_{K_4Fe(CN)_6}$ denote the arithmetic means of the D-values for the respective component ions, and x is the fraction of the total ionic strength μ corresponding to KCl. With decreasing x, f_1/f_0 increases and attains a finite limiting value which refers to the activity coefficient of KCl when present in very small amount in an aqueous solution of $K_4Fe(CN)_6$. As D is given by Debye and Hückel as a function of r (cf. *Physikal. Zeitsch.* p. 195, 1924), it is possible to calculate f_1/f_0 in this limiting case, assuming that the size of the $Fe(CN)_6$ ion is extremely large compared with those of the Cl ion and K ion, and taking (as Debye and Hückel do) $a_{Cl} = a_K = 3.76 \times 10^{-8}$. In this way we can calculate that the limiting value of the ratio f_1/f_0 for KCl in

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[*] In this equation the effect due to change of the dielectric constant of the solution is omitted.

a 0·1 normal solution of $K_4Fe(CN)_6$ is 1·076. Thus the effect of the relative size of the $Fe(CN)_6$ ion on the activity-coefficient of KCl might possibly account for a part of the observed deviation from the Lewis ionic strength principle.

3. *New Experiments.*

A new series of experiments on the distribution of potassium chloride (across a copper ferrocyanide membrane) between a pure solution of potassium chloride and a mixed solution of potassium chloride and ferrocyanide was carried out in order to determine, if possible, whether any measurable deviation from the ionic strength principle exists in this case.

Method of Analysis.

The analytical method employed by Donnan and Allmand was the titration of chloride plus ferrocyanide with silver nitrate, using potassium chromate as indicator, and the titration of the ferrocyanide in another sample of the same solution by means of potassium permanganate. The chloride is thus determined by difference. An examination of this method showed that the silver nitrate titration gives correct results if a dilute solution is used and if the titration is done slowly with constant stirring. Otherwise too low a value is often found for the chloride. Another drawback is that in the indirect determination of the chloride any errors in the permanganate titration are considerably multiplied. On the whole the method was found unreliable when the ratio of chloride to ferrocyanide in the solution was relatively small. It was decided, therefore, that in order to obtain accurate results a direct method of estimating the chloride in the mixed solution must be used. After a lengthy testing of various possible methods, the following one was found to give accurate results. The ferrocyanide is removed by precipitation with zinc sulphate solution and the chloride estimated directly in the filtrate and washings. Decinormal zinc sulphate solution is allowed to drop slowly from a burette into the solution kept stirred at 50°–60°. The solution and precipitate are allowed to stand at room temperature overnight, and then the precipitate is filtered off and washed with 0·02 N zinc sulphate solution. Usually a clear solution is obtained in the first filtration, but sometimes a second one is necessary. The chloride in the mixed filtrate and washings is then titrated electrometrically with decinormal silver nitrate solution, using a silver electrode

against a normal calomel electrode, the end point being determined by the maximum change of E.M.F. per drop of the titrating solution. Neither the excess of zinc sulphate nor the potassium sulphate present in the solution was found to affect the accuracy of the result. The ferrocyanide in the mixed solution was estimated by titration with decinormal permanganate solution. In the pure solutions of potassium chloride the chloride was titrated electrometrically as described above. It may be of some interest to mention here that an attempt was made to estimate both chloride and ferrocyanide by a single electrometric titration with silver nitrate solution and silver electrode. Although the end point for the sum of chloride plus ferrocyanide was found to be sharp and accurate, the change over of silver ferrocyanide into silver chloride was not rapid enough. An attempt was also made to titrate the ferrocyanide electrometrically by decinormal zinc sulphate solution, using a platinum electrode combined with the addition of some ferrocyanide, and to use the filtrate for the estimation of chloride. Although the end point of the ferrocyanide titration was found to be sharp and accurate, the estimation of chloride in the filtrate gave results which were a little too high, owing to the solubility of zinc ferricyanide, which is higher than that of the ferrocyanide.

Distribution Apparatus and Method.

The solutions were contained in cylindrical vessels of lead glass of 100 c.c. capacity, clamped tightly together. The parchment membrane, about 40 sq. cm. in area, was held between the ground flanges of the two vessels by means of annular rubber washers. A thin multi-perforated ebonite plate was pressed against each side of the membrane. The vessel containing the pure potassium chloride carried a pair of platinum electrodes, the tubes of which passed through a paraffined rubber stopper fitted into a vertical side tube. The object of the platinum electrodes was to ascertain, by means of measurements of electrical conductivity, when distribution equilibrium was attained. It was found that, if the perforated ebonite disks were not used, bulging of the membrane due to slight osmosis changed the cell constant and made the conductivity measurements unreliable. When experience with these special vessels had shown the time required for the attainment of distribution equilibrium, other vessels (of Jena glass) without electrodes and without ebonite plates were also employed.

The membranes were prepared by stretching tightly a

sheet of vegetable parchment across a wide and shallow glass cylinder, and keeping it between an 0·2 N copper sulphate solution and an 0·2 N potassium ferrocyanide solution. After washing the membrane, the solutions were interchanged every day, and this was continued for four or five days, after which the membrane was well washed and kept under water until required. Every care was taken to avoid oxidation of the ferrocyanide. The solutions were made up from water which had been boiled and cooled in a stream of nitrogen, and the air remaining in the side tubes of the compartment vessels was replaced by nitrogen. At the completion of the experiments (*i. e.* attainment of distribution equilibrium), the solutions gave no colour reaction with phenolphthalein, showing that neither oxidation nor hydrolysis had occurred.

The side tubes of the vessels were closed by means of rubber pressure tubing and glass rods. The object of this was to exclude air and to enable osmotic equilibrium to be attained quickly without much osmotic transference of water. The vessels were kept in an air thermostat at $25° \pm 0·1°$, and the contents of each compartment were mixed once every day by inverting the apparatus (stirring being effected by means of the gas bubble in the side tube).

Experimental Results.

The results obtained and the values calculated therefrom are shown in Table II. and fig. 2.

Concentrations are expressed in milli equivalents per litre and the symbols have the same meanings as in Table I. In confirmation of the results obtained by Donnan and Allmand, it is seen that the ionic strength principle holds well when the chloride concentration is not small in comparison with that of the ferrocyanide. When the chloride concentration is relatively small, a comparison of the first five experiments of Series I. and II. (Table II.) with experiments Nos. 17, 18, 29, and 30 (Donnan and Allmand, Table I.) shows that the ionic strength principle holds good also in these cases. A comparison of the first four experiments of Series III. in Table II. with experiments Nos. 39 and 40 of Table I. is not strictly justified, since in the former case the ferro-cyanide is somewhat more dilute and the chloride more concentrated. There is no evidence, however, in the present experiments with the most concentrated solution of potassium ferrocyanide (Series III. of Table II.) that this electrolyte *increases* the activity coefficient of potassium chloride in a

TABLE II.

	B.	C.	D.	E.	F.	G.	H.	L.	
	Solution 1.		Sol. 2.						
A. Exp. No.	$K_4Fe(CN)_6$	KCl	KCl	$\frac{m_2}{m_1}$	f_2	$\mu_1^{\frac{1}{2}}$	f_1	f_c	$\frac{f_1}{f_0}$
1	19·8	12·3	16·4	0·933	0·901	0·2105	0·841	0·848	0·992
2	19·1	10·3	16·2	0·931	0·902	0·2408	0·839	0·830	1·011
3	18·9	11·4	16·8	0·906	0·900	0·2423	0·813	0·830	0·980
4	18·2	11·5	16·8	0·901	0·900	0·2383	0·818	0·832	0·983
5	18·7	11·9	17·4	0·912	0·899	0·2423	0·819	0·830	0·987
6	17·8	22·2	27·8	0·932	0·876	0·2583	0·817	0·821	0·995
7	18·3	22·1	28·0	0·936	0·876	0·2606	0·820	0·820	1·000
8	18·9	22·3	27·8	0·917	0·875	0·2638	0·802	0·818	0·981
9	19·2	45·4	51·0	0·942	0·839	0·3056	0·790	0·799	0·990
10	18·1	46·6	52·3	0·975	0·837	0·3031	0·816	0·800	1·021
11	16·5	108·9	113·9	0·975	0·785	0·3874	0·765	0·768	0·996
12	16·3	118·7	123·5	0·977	0·780	0·3995	0·761	0·764	0·996
13	18·1	212·4	216·2	0·978	0·744	0·5077	0·727	0·731	0·995

Series I.
$K_4Fe(CN)_6$
ca. 0·018 N.

TABLE II. (*continued*)

Exp. No.	Solution 1. $K_4Fe(CN)_6$	Solution 1. KCl	Sol. 2. KCl	$\dfrac{m_2}{m_1}$	f_2	$\mu_1^{\frac{1}{2}}$	f_1	f_3	$\dfrac{f_1}{f_0}$
	B.	**C.**	**D.**	**E.**	**F.**	**G.**	**H.**	**L.**	**J.**
1	43·6	9·6	19·4	0·857	0·894	0·3444	0·766	0·782	0·979
2	45·3	9·5	19·5	0·867	0·893	0·3504	0·773	0·780	0·992
3	40·1	10·9	20·6	0·873	0·891	0·3334	0·779	0·787	0·989
4	42·4	10·7	20·9	0·877	0·890	0·3416	0·780	0·784	0·996
5	40·8	11·0	21·6	0·905	0·889	0·3362	0·804	0·786	1·023
6	41·4	14·5	24·2	0·850	0·883	0·3436	0·751	0·783	0·959
7	42·4	14·9	25·7	0·880	0·880	0·3477	0·774	0·782	0·990
8	41·2	15·4	25·9	0·877	0·880	0·3442	0·771	0·783	0·985
9	46·9	16·5	28·2	0·871	0·875	0·3658	0·763	0·776	0·984
10	34·2	29·9	39·7	0·906	0·854	0·3398	0·774	0·785	·987
11	44·9	43·7	56·7	0·912	0·832	0·3950	0·758	0·766	0·990
12	35·0	48·2	59·3	0·936	0·829	0·3684	0·776	0·769	1·009
13	40·0	87·5	99·5	0·943	0·794	0·4380	0·748	0·754	0·992

Series II.
$K_4Fe(CN)_6$
ca. 0·4 N.

TABLE II. (*continued*).

A.	B.		C.	D.	E.	F.	G.	H.	I.	J.
	Solution 1.			Sol. 2.						
Exp. No.	$K_4Fe(CN)_6$.		KCl.	KCl.	$\frac{m_2}{m_1}$	f_2	$\mu_1^{\frac{1}{2}}$	f_1.	f_0	$\frac{f_1}{f_0}$
1	72·0		12·0	25·7	0·809	0·880	0·438	0·712	0·752	0·947
2	80·3		11·1	26·0	0·816	0·880	0·460	0·718	0·746	0·963
3	82·2		10·7	26·1	0·828	0·879	0·465	0·728	0·744	0·978
4	82·3		10·7	26·9	0·853	0·878	0·465	0·748	0·744	1·006
5	71·6		18·0	33·6	0·837	0·865	0·444	0·723	0·750	0·964
6	77·8		18·7	35·6	0·838	0·861	0·462	0·721	0·745	0·963
7	81·5		27·1	45·4	0·837	0·846	0·481	0·703	0·740	0·957
8	74·5		35·1	53·8	0·867	0·836	0·471	0·725	0·744	0·975
9	83·9		45·0	66·7	0·876	0·823	0·505	0·721	0·732	0·985
10	73·3		47·7	67·0	0·882	0·823	0·481	0·725	0·740	0·980
11	79·1		89·9	111·1	0·901	0·787	0·536	0·709	0·722	0·982
12	81·9		224·1	245·6	0·938	0·735	0·655	0·690	0·693	0·995

Series III.
$K_4Fe(CN)_6$
ca. 0·08 N.

manner which is not accounted for by the Lewis principle of ionic strength. It is probable, therefore, that the aberrant results calculated from certain of the experiments of Donnan and Allmand are due to experimental error.

Fig. 2.
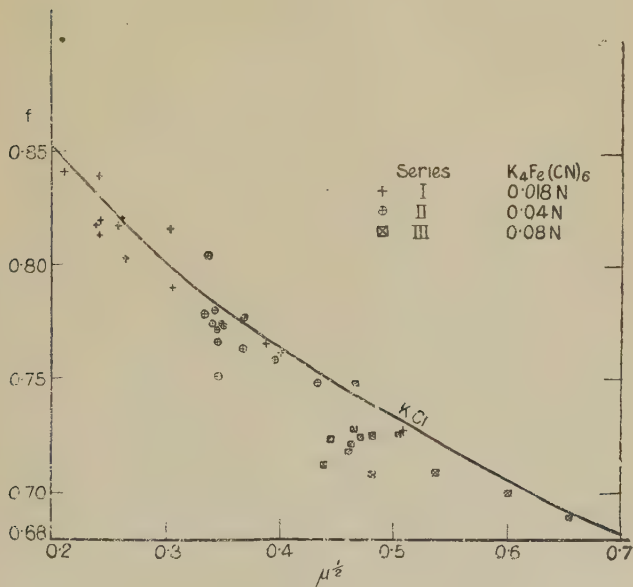
Summary.

1. The experiments of Donnan and Allmand on the unequal distribution of potassium chloride across a copper ferrocyanide membrane between a pure aqueous solution and one containing potassium ferrocyanide have been recalculated and discussed from the point of view of activity and the ionic strength principle of G. N. Lewis

2. It has been shown that, except when the potassium chloride concentration is small in comparison with that of the ferrocyanide, the results of the distribution equilibrium experiments of Donnan and Allmand are in agreement with the ionic strength principle.

3. New experiments carried out with a more reliable method of analysis and an improved technique render it

probable that the marked deviations from the ionic strength principle referred to in (2) are due to experimental errors.

In conclusion the author desires to express his best thanks for advice and assistance to Professor F. G. Donnan, at whose suggestion the investigation was undertaken.

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      March, 1925.

XCIV. *Three Examples illustrating X-Ray Methods of supplementing and correcting Crystallographic Data.* By KATHLEEN YARDLEY, *M.Sc.**

THE three crystalline substances discussed in this paper are all derivatives of maleic or fumaric acids, and they were at first chosen for X-ray examination mainly because of their chemical interest. Subsequently, however it became apparent that these substances illustrate well the difficulty of determining accurately the dimensions and symmetry of the true unit cell of any crystal using purely crystallographic methods, and that they show also to what extent X-ray investigation can supplement or correct results obtained by means of the older methods.

The "reflexions" of an X-ray beam take place, not necessarily from faces, but also from planes within the crystal, so that for X-ray work a well-developed crystal is not always required. When the powder method of X-ray analysis is adopted, the crystalline substance may be ground very fine ; and even on the Bragg spectrometer complete crystallographic measurements can be obtained for crystals showing no plane faces †. But as a general rule the best observations are made on small good crystals, equally well adapted for the usual goniometric examination. If previous goniometric measurements are available, the task of the X-ray worker is considerably lightened. Such measurements decide the system and, in general, the class to which the crystals belong. They cannot fix the Bravais lattice (except in the triclinic system, where only one lattice is possible) nor the space-group. On the other hand, X-ray measurements can decide the system and the

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Bravais lattice upon which the structure is founded, and, given the class, can also fix the space-group. But since the X-rays always add a centre to the elements of symmetry already possessed by a crystal, their usefulness in determining the class is to that extent strictly limited. That is to say, they can distinguish between all the classes already possessing centro-symmetry, but cannot, in general, discriminate between those with a centre of symmetry and those without.

Again, the usual goniometric measurements lead to an axial ratio and axial angles for any given crystal, thus fixing the relative lengths and the orientations of the edges of a possible unit cell. They cannot, however, decide the absolute dimensions of the cell; nor is it possible, in the case of the lower classes of symmetry, to state definitely that the unit cell chosen is even similar in shape to the true minimum cell. A good working definition of the true minimum cell is that it is " the smallest portion of a crystal which, repeated through space without change of character or orientation, makes up the crystal " *. In the triclinic system there are, of course, an infinite number of possible minimum cells, all having the same volume ; in practice the cell chosen is that which, fulfilling the above definition, has its axial angles most nearly equal to right angles. Similarly, in the monoclinic system, the direction of one axis is definitely fixed as being parallel to the axis of symmetry or normal to the plane of symmetry. The other two axes are generally chosen to be as nearly as possible at right angles to each other, in so far as this is compatible with the law of integral indices. But this is not sufficient : for the unit cell so chosen to be the minimum cell, it must also comply with the above definition.

Using X-rays, the minimum cell can be definitely found even in the case of a triclinic crystal, and more easily in the case of more symmetrical crystals. Considering the difficulty of determining the relative dimensions of the true unit cell from external measurements alone in the case of crystals of low symmetry, it is not surprising that the axial ratio and angles given as a result of previous goniometric work are occasionally found to need amendment when the true minimum cell is revealed by an X-ray analysis.

The following measurements were made on the Bragg

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* 'X-Rays and Crystal Structure,' W. H. Bragg and W. L. Bragg.

spectrometer, using a Coolidge tube of rhodium anti-cathode :—

A. *Potassium hydrogen chlormaleate.*

$$[C_2 . HCl . COOH . COOK.]$$

The method of preparing this substance was first described by Perkin, and the crystals were measured by Haushöfer [*]. They grow as colourless pseudo-hexagonal plates on {001}, bounded by {111} and {021}. Many of the crystals were elongated in the direction of the a axis, and on some the {010} faces were developed, though small. Groth [†] described them as

Rhombic bipyramidal.

$$a : b : c = 0\cdot4841 : 1 : 0\cdot3479$$

The relative density (ρ) was measured by suspension in a mixture of benzene and methylene iodide, and was found to be $1\cdot894$ at $19°/4°$ C. The constitution of the molecule shows that the molecular weight (M) is $188\cdot6$.

By means of the two formulæ,

$$a . b . c . \rho = n . M . 1\cdot65$$

and

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2},$$

the spacing (d) of any plane having indices ($h\,k\,l$) may be calculated, assuming a definite number of molecules (n) per unit cell. It was found that by taking $n = 4$ many of the calculated spacings agreed with the measured values. Others, however, were either twice or one-half as large as the measured values. The comparison is made in the second and third columns of the following table.

Now in an orthorhombic crystal it is almost impossible that the directions of the axes should have been incorrectly chosen. If, however, any of the measured spacings are multiples of the calculated spacings, then it is obvious that the unit cell chosen is too small and that one or more of the axes a, b, c should be increased in order to obtain the true minimum cell. By referring to columns 1, 2, and 3 of

* Perkin, Journ. Chem. Soc. Lond. (1888) liii. p. 707.
† Groth, *Chemische Krystallographie*, iii. p. 288.

TABLE I.

1. $\{hkl\}$ referred to original cell.	2. Spacing: calc. from original cell.	3. Measured Spacing.	4. Spacing: calc. from true cell.	5. $\{hkl\}$ referred to true cell.	6. Relative intensity of measured reflexions.
$\{010\}$	15·74	7·85	15·74	$\{010\}$	II M.S.; IV M.W.
$\{081\}$	1·85	1·85	3·70	$\{041\}$	II M.W.
$\{061\}$	2·36$_5$	4·71	4·73	$\{031\}$	I M.
$\{041\}$	3·20	3·19	6·40	$\{021\}$	II M.W.
$\{0103\}$	1·19	2·36	2·38	$\{053\}$	I V.W.
$\{021\}$	4·49$_5$	8·97	8·99	$\{011\}$	I W.; III M.S.
$\{001\}$	5·47$_5$	5·44	10·95	$\{001\}$	II W.; IV M.W.
$\{100\}$	7·62	3·81	7·62	$\{100\}$	II M.S.
$\{210\}$	3·70	3·71	3·70	$\{210\}$	I M.
$\{110\}$	6·86	3·49	6·86	$\{110\}$	II W.
$\{120\}$	5·47$_5$	2·74	5·47$_5$	$\{120\}$	II M.W.
$\{130\}$	4·32	2·16	4·32	$\{130\}$	II M.W.
$\{401\}$	1·80	3·61	3·60	$\{201\}$	I M.W.
$\{301\}$	2·30	2·32	2·30	$\{302\}$	I M.S.
$\{201\}$	3·13	6·26	6·26	$\{101\}$	II S.; III W.
$\{101\}$	4·45	4·44	4·45	$\{102\}$	I M.S.
$\{111\}$	4·28	4·28	4·28	$\{112\}$	I M.
$\{441\}$	1·63$_5$	3·22	3·27	$\{221\}$	I W.
$\{421\}$	1·75$_5$	3·53	3·51	$\{211\}$	I W.
$\{121\}$	3·87	3·89	3·87	$\{122\}$	I M.W.
$\{263\}$	1·39$_5$	2·76	2·79	$\{133\}$	I M.W.

Table I., it will be seen that

(a) The measured spacings are twice the calculated spacings for all planes $\{hkl\}$ where h and k are even and l is an odd integer (zero counting as an even integer), except in the special case where h is zero and k a multiple of 4.

(b) There are, however, no doubled spacings for planes having indices $\{hk0\}$; on the contrary, the measured spacings are only one-half of the calculated for such planes if h is odd.

(c) In addition, the measured spacing of the $\{010\}$ is one-half of the calculated.

The last two facts, (b) and (c), show that the relative lengths of the a and b axes are correct, since no doublings occur for planes $\{hk0\}$ and the halvings observed may be completely explained on the space-group theory. The observations included under (a) may be completely explained by the assumption that the c axis of the original cell is only half the length of the c axis of the true minimum cell. In that case, the correct axial ratio should be

$$a : b : c = 0{\cdot}4841 : 1 : 0{\cdot}6958,$$

and the true minimum cell contains 8 molecules.

The original cell, repeated parallel to itself through space, would not build up the correct structure ; it would have to be combined with its own reflexion in a glide-plane of symmetry in order to do so. The original cell together with its reflexion in a glide-plane parallel to the $\{001\}$ constitute the true minimum cell. The result of multiplying the c axis by 2 is that the calculated spacings of all planes having indices of the form $\{$even, even, odd$\}$ must also be multiplied by 2, all others remaining unaltered. Also the true indices of the planes may be obtained by multiplying the l index by 2, so that $\{11\bar{1}\}$ becomes $\{112\}$, $\{041\}$ becomes $\{021\}$, and so on.

Columns 4 and 5 of Table I. show the spacings calculated from the true minimum cell, and the true indices of the planes. Referring now to the true cell we see that

(a) The measured spacings are half the calculated for all planes with indices $\{hk0\}$ where h is odd, and $\{0kl\}$ where $(k+l)$ is odd—that is, all odd-order reflexions of the full spacing are absent for such planes.

(b) All other planes show normal spacings.

The halvings given in (a) show that the Bravais lattice is the simple lattice Γ_o, and the space-group is Q_h^{16} *. The eight molecules contained in the minimum cell are all asymmetric. . In column 6 the relative intensities of

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* W. T. Astbury and K. Yardley, Phil. Trans. Roy. Soc. A, ccxxiv. p. 221.

reflexion of various orders are given: the Roman numerals indicate the orders referred to the true calculated spacing; the letters have the following meanings :—

V.S.I. Very strong indeed.
V.S. Very strong.
S. Strong.
M.S. Moderately strong.
M. Moderate.
M.W. Moderately weak.
W. Weak.
V.W. Very weak.

It will be seen that the planes occurring as crystal faces are not necessarily those giving the strongest reflexions of X-rays. The occurring forms, referred to the true unit cell, are $\{001\}$, $\{112\}$, $\{01\bar{1}\}$, and $\{010\}$. The crystal used in this investigation measured about $4 \times 2 \times 1$ mm.

B. *Ammonium chlorfumarate.*

$$[C_2 \cdot HCl \cdot (COONH_4)_2.]$$

This substance was also first prepared by Perkin [*], and the crystals were measured by Muthmann [†]. They are colourless prisms bounded by $\{110\}$, $\{100\}$, and occasionally $\{010\}$ (small), with end faces $\{001\}$ and $\{10\bar{1}\}$. In the original description [*] they are merely stated to be "mono-symmetrical," but Groth [‡] describes them as

Monoclinic prismatic.

$$a : b : c = 1\cdot 3892 : 1 : 1\cdot 0059,$$
$$\beta = 108^\circ 48'.$$

There is an excellent cleavage parallel to $\{010\}$. A density determination made as for A gave $\rho = 1\cdot 532$ at $18^\circ\cdot 5/4^\circ$ C. The molecular weight (M) corresponding to the chemical formula given above is $184\cdot 5$. The spacing (d) of any plane $\{hkl\}$ may be calculated by means of the two formulæ :

$$a \cdot b \cdot c \cdot \rho \cdot \sin \beta = n \cdot M \cdot 1\cdot 65,$$

and

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \left(\frac{l}{c \sin \beta} - \frac{h}{a \tan \beta} \right)^2.$$

Assuming $n = 2$, we find the following agreement between measured and calculated spacings (Table II.) :—

[*] Perkin, *loc. cit.* p. 699.
[†] Muthmann, *Zeit. f. Kryst.* (1889) xv. p. 395.
[‡] Groth, *loc. cit.* p. 285.

TABLE II.

$\{hkl\}$.	Spacing calculated.	Spacing measured.	Relative intensity of reflexion.
$\{100\}$	8·81	8·82	I W.; II M.; III M.
$\{010\}$	6·70	3·35 †	II V.S.; IV W.
$\{110\}$	5·33	5·35	I M.
$\{210\}$	3·68	3·71	I M.
$\{310\}$	2·68	2·70	I M.
$\{430\}$	1·56	1·58	I W.
$\{120\}$	3·13	3·15	I M.S.
$\{130\}$	2·16	2·18	I M.
$\{140\}$	1·64	1·65	I W.
$\{001\}$	6·38	6·36	I M.; II M.S.
$\{013\}$	2·02	2·02	I W.
$\{012\}$	2·87	2·86	I W.
$\{023\}$	1·79	1·79	I W.
$\{011\}$	4·62	4·63	I M.S.
$\{021\}$	2·96	2·98	I M.W.
$\{031\}$	2·11	2·12₅	I W.
$\{041\}$	1·62	1·62	I V.W.
$\{30\bar{1}\}$	3·07	3·06	I V.W.
$\{301\}$	2·39	2·40	I M.
$\{20\bar{1}\}$	4·34	4·36	I V.W.
$\{201\}$	3·18	3·19	I W.
$\{30\bar{2}\}$	2·62	2·61	I M.W.
$\{10\bar{1}\}$	6·20	6·20	I M.
$\{101\}$	4·52	4·59	I W.
$\{20\bar{3}\}$	2·21	2·21	I V.W.
$\{203\}$	1·71	1·71	I V.W.
$\{10\bar{2}\}$	3·37	3·38	I M.W.
$\{102\}$	2·72	2·74	I M.W.
$\{10\bar{3}\}$	2·23	2·23	I M.W.
$\{103\}$	1·92₅	1·94	I V.W.
$\{111\}$	3·75	3·74₅	I W.
$\{112\}$	2·52	2·52₅	I V.W.
$\{113\}$	1·85	1·89	I V.W.
$\{221\}$	2·30	2·30	I W.
$\{11\bar{2}\}$	3·01	3·00	I M.W.
$\{11\bar{1}\}$	4·55	4·55	I M.
$\{12\bar{1}\}$	2·94	2·96	I M.W.
$\{21\bar{2}\}$	2·81	2·81	I M.
$\{31\bar{3}\}$	1·97	1·96	I W.
$\{14\bar{1}\}$	1·61	1·63	I W.
$\{31\bar{2}\}$	2·44	2·42	I V.W.

The mean value found for the angle β was $108° \ 25'$, as against the previous value of $108° \ 48'$. It will be seen that all the values found agree with those calculated, except for the plane (010). This plane shows a halved spacing, indicating that the space-group is C_{2h}^2 *—that is, if the crystal class is really monoclinic prismatic. But in that case each molecule, since there are only two in the unit cell, would have to possess two-fold symmetry—either a plane or a centre *. Now it is almost impossible for a molecule having the structural formula
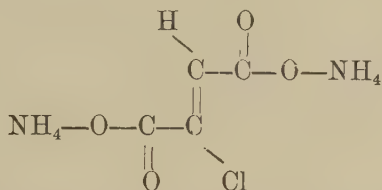
to possess either a plane or a centre of symmetry. It must be asymmetric, unless all the atoms (except the hydrogens of the ammonium groups) lie in a plane, which in that case might be a plane of symmetry. But this is a most improbable arrangement. It is far more likely that the two molecules are asymmetric and combine about a plane or an axis to form a monoclinic domatic or a monoclinic sphenoidal cell. Unfortunately, it is impossible by means of X-rays to distinguish directly between the three monoclinic classes, since the X-rays always add a centre to the symmetry already possessed by the crystals. Indirectly, however, it is sometimes possible to deduce that one class is more probable than another. In this case, for example, since there are only two molecules in the unit cell and the molecules are almost certainly asymmetric, either the domatic or the sphenoidal class is more likely than the prismatic. Again, in the domatic class one would expect either no halvings at all or else sets of planes halved, but in the sphenoidal class for crystals built up on the simple Bravais lattice Γ_m the only plane whose spacing could be halved would be the (010). This crystal is certainly built up on that simple lattice (since no doublings or halvings were found among planes (hkl) with no zero index) and the (010) spacing only is halved. This, therefore, points to the sphenoidal as the most probable class, and to C_2^2 as the correct space-group. It is worth noticing that the

* W. T. Astbury and K. Yardley, *loc. cit.*

strongest reflexion was found for the cleavage plane. This is often the case, since such planes are generally closely packed with atoms and very few atoms lie between the successive planes.

C. *Ammonium hydrogen fumarate.*
$$[C_2H_2 . COO(NH_4) . COOH.]$$

The goniometric measurements on these triclinic pinakoidal crystals were made by Repossi *, who gave as the observed forms: $\{100\}$, $\{010\}$, $\{110\}$, $\{011\}$, $\{111\}$, $\{1\bar{1}\bar{1}\}$, $\{131\}$, $\{13\bar{1}\}$, $\{\bar{1}31\}$, $\{311\}$. Frequent twinning takes place on $\{100\}$. There is a good cleavage parallel to $\{100\}$ and a very imperfect cleavage parallel to $\{1\bar{1}\bar{1}\}$. The crystallographic elements are quoted by Groth † as

$$a : b : c = 0.8587 : 1 : 0.4558,$$

$$\alpha = 81° \ 10\tfrac{1}{2}', \quad \beta = 89° \ 59\tfrac{3}{4}', \quad \gamma = 75° \ 17\tfrac{3}{4}',$$

For the purposes of calculation and comparison with measured values these angles are taken to the nearest minute, since no further accuracy would be at all justifiable.

The density was measured as before and found to be 1·574 grs./c.c. at 18°/4° C. The molecular weight corresponding to the chemical formula is 133·1. The formulæ used for the calculation of the actual lengths of the axes and the spacing (d) of any plane (hkl) now assume their most general form:

$$a . b . c . N . \rho = n . M . 1·65,$$

$$\frac{N^2}{d^2} = \sum \frac{h^2}{a^2} \sin^2 \alpha + 2 \sum \frac{kl}{bc} (\cos \beta \cos \gamma - \cos \alpha),$$

where

$$N = 4 \sin \tfrac{1}{2}(\alpha + \beta + \gamma) \sin \tfrac{1}{2}(-\alpha + \beta + \gamma)$$
$$\sin \tfrac{1}{2}(\alpha - \beta + \gamma) \sin \tfrac{1}{2}(\alpha + \beta - \gamma).$$

In this case, since $\beta = 90°$ (very nearly), the second formula simplifies considerably and becomes

$$\frac{N^2}{d^2} = \frac{h^2}{a^2} \sin^2 \alpha + \frac{k^2}{b^2} + \frac{l^2}{c^2} \sin^2 \gamma - 2\frac{kl}{bc} \cos \alpha$$
$$+ 2\frac{lh}{ca} \cos \gamma \cos \alpha - 2\frac{hk}{ab} \cos \gamma.$$

---

* Repossi, *Rend. Accad. Lincei Rom.* 1904, (5) xiii. ii. p. 468.   Also *Zeitschr. f. Kryst.* xli. p. 61.

† Groth, *Chemische Krystallographie,* iii. p. 284.

TABLE III.

1. $\{hkl\}$ referred to original cell.	2. Spacing: calc. from original cell.	3. Measured Spacing.	4. Relative intensity of reflexion.	5. Spacing: calc. from true cell.	6. $\{h'k'l'\}$ referred to true cell.
$\{100\}$	$5\cdot97$	$5\cdot98$	II V.S.I.	$5\cdot97$	$\{100\}$
$\{010\}$	$6\cdot87_5$	$6\cdot88$	II M.W.	$6\cdot87_5$	$\{010\}$
$\{120\}$	$3\cdot38$	$3\cdot41$	V.W.	$3\cdot38$	$\{120\}$
$\{1\bar{2}0\}$	$2\cdot69_5$	$2\cdot71$	W.	$2\cdot69_5$	$\{1\bar{2}0\}$
$\{1\bar{3}0\}$	$1\cdot95_5$	$1\cdot99$	W.	$1\cdot95_5$	$\{1\bar{3}0\}$
$\{1\bar{1}0\}$	$4\cdot02_5$	$4\cdot02$	II V.W.	$4\cdot02_5$	$\{1\bar{1}0\}$
$\{210\}$	$3\cdot04$	$3\cdot03_5$	W.	$3\cdot04$	$\{210\}$
$\{2\bar{1}0\}$	$2\cdot51$	$2\cdot52$	W.	$2\cdot51$	$\{2\bar{1}0\}$
$\{310\}$	$2\cdot08$	$2\cdot06$	V.W.	$2\cdot08$	$\{310\}$
$\{101\}$	$2\cdot80$	$2\cdot77$	W.	$2\cdot80$	$\{0\bar{1}2\}$
$\{1\bar{1}1\}$ *	$2\cdot39$	$4\cdot76$	M.W.	$4\cdot78$	$\{0\bar{1}1\}$
$\{121\}$	$2\cdot51$	$2\cdot50$	M.S.	$2\cdot51$	$\{012\}$
$\{131\}$ *	$2\cdot05$	$4\cdot10_5$	M.S.	$4\cdot10$	$\{011\}$
$\{1\bar{3}1\}$ *	$1\cdot58_5$	$3\cdot13$	V.W.	$3\cdot17$	$\{0\bar{2}1\}$
$\{151\}$ *	$1\cdot38_5$	$2\cdot76$	V.W.	$2\cdot77$	$\{021\}$
$\{1\bar{5}1\}$ *	$1\cdot12_5$	$2\cdot24$	M.	$2\cdot25$	$\{0\bar{3}1\}$
$\{011\}$	$3\cdot13$	$3\cdot10$	M.W.	$3\cdot13$	$\{\bar{1}02\}$
$\{111\}$ *	$2\cdot86$	$5\cdot74$	S.	$5\cdot72$	$\{001\}$
$\{\bar{1}11\}$ *	$2\cdot69$	$5\cdot36$	M.W.	$5\cdot38$	$\{\bar{1}01\}$
$\{311\}$ *	$1\cdot74$	$3\cdot46$	V.S.	$3\cdot48$	$\{101\}$
$\{\bar{3}11\}$ *	$1\cdot62$	$3\cdot24$	V.S.	$3\cdot24$	$\{\bar{2}01\}$
$\{10\bar{1}\}$	$2\cdot90$	$2\cdot89$	M.	$2\cdot90$	$\{21\bar{2}\}$
$\{12\bar{1}\}$	$2\cdot20$	$2\cdot19$	W.	$2\cdot20$	$\{23\bar{2}\}$
$\{13\bar{1}\}$ *	$1\cdot78$	$3\cdot55$	S.	$3\cdot56$	$\{12\bar{1}\}$
$\{\bar{1}31\}$ *	$1\cdot81$	$3\cdot62$	V.S.	$3\cdot62$	$\{\bar{1}11\}$
$\{31\bar{3}\}$ *	$\cdot95_5$	$1\cdot90$	W.	$1\cdot91$	$\{32\bar{3}\}$
$\{\bar{3}13\}$ *	$\cdot96$	$1\cdot91$	W.	$1\cdot92$	$\{\bar{3}13\}$
$\{11\bar{1}\}$ *	$2\cdot65$	$5\cdot30$	W.	$5\cdot30$	$\{11\bar{1}\}$
$\{01\bar{1}\}$	$2\cdot76_5$	$2\cdot77$	W.	$2\cdot76_5$	$\{12\bar{2}\}$
$\{231\}$	$1\cdot86$	$1\cdot86$	V.W.	$1\cdot86$	$\{122\}$
$\{1\bar{1}3\}$ *	$1\cdot00_5$	$2\cdot01$	M.W.	$2\cdot01$	$\{\overline{123}\}$
$\{3\bar{3}1\}$ *	$1\cdot19$	$2\cdot38$	M.W.	$2\cdot38$	$\{1\bar{2}1\}$
$\{53\bar{1}\}$ *	$1\cdot10_5$	$2\cdot21$	M.	$2\cdot21$	$\{32\bar{1}\}$

It was found that by taking $n = 1$ a considerable number of the calculated spacings agreed with the measured values. The measured spacings of planes having all odd indices were, however, invariably twice the calculated values. Such planes, too, were very largely in evidence, and the reflexions from them were unusually strong. This is seen in columns 1, 2, 3, 4 of Table III.

The relative intensities refer to the I[st] order reflexion, except where otherwise stated. The fact that only IInd orders were found for the {100}, {010}, and {110} planes

Fig. 1.
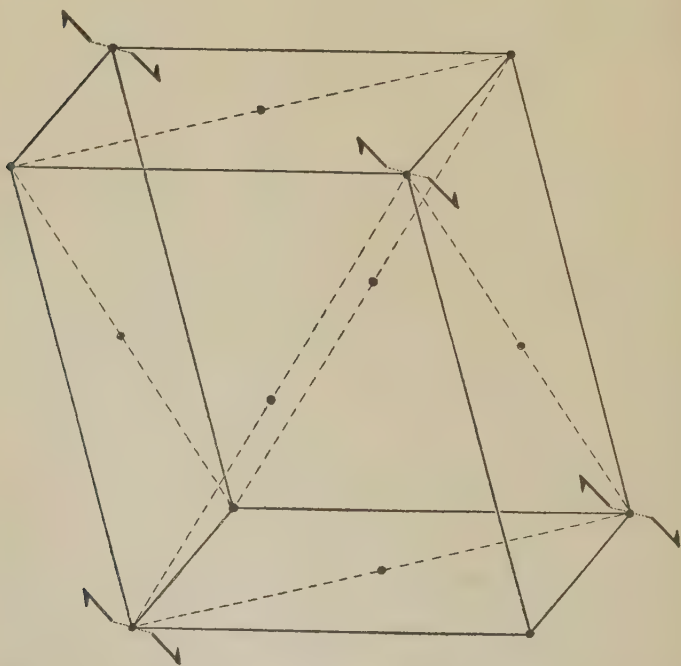
can have no geometrical meaning in the triclinic system, though it may be an indication of the relative positions of differently orientated molecules. The fact that double spacings were found only for "all odd" planes tells us immediately how the true unit cell (or rather one of an infinite number of such minimum cells) is related to the original crystallographic cell. It shows that, if we doubled all the original axes, the cell so obtained, occupying eight times the volume of the original cell, would be face-centred

and would contain 8 molecules. In other words, the corners of the original cell are not similar ; every corner is the centre of gravity of two molecules arranged centro-symmetrically about it, and there are also centres of symmetry at the midpoints of the faces, but not at the midpoints of the edges, as there should be in a true unit cell. Fig. 1 represents the original cell, the half-arrows denoting asymmetric molecules and the dots centres of symmetry. It is clear that each (111) plane, for example, differs from the next but is similar to the next but one. Thus the spacing of the (111) and other " all odd " planes

Fig. 2.
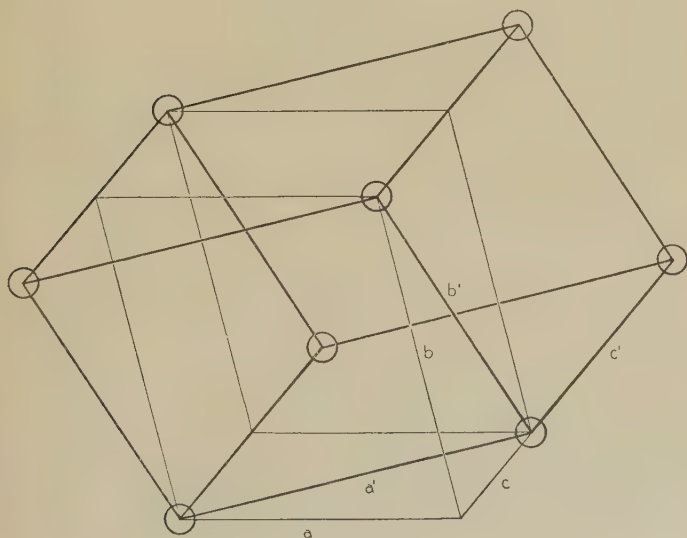
should be found doubled, as is actually the case. There are a variety of ways in which the true unit cell might be regarded. That aspect has been chosen which retains the original (100) and (010) planes and in which the old (111) plane (which gave a strong X-ray reflexion) is the new (001) plane.

In the accompanying fig. 2 is seen the relationship between the original cell (thin lines) and the new cell (thick lines). For the sake of simplicity each *pair* of molecules, centro-symmetrically connected in fig. 1, has been represented by a single open circle in fig. 2. Thus the new unit cell contains two asymmetric molecules, and

its axes a', b', c' are connected with the original cell as follows :—

   a' is the shorter diagonal of the original (010) face.
   b' ,,   ,,   ,,   ,,   (100) ,,
   c' is parallel to the original c axis, and $c' = 2c$.

The crystallographic elements of the new cell are :

$$a' : b' : c' = 0{\cdot}9409 : 1 : 0{\cdot}8822,$$

$$\alpha' = 107^\circ\, 1', \quad \beta' = 117^\circ\, 58', \quad \gamma' = 69^\circ\, 16'.$$

Hence
$$\left.\begin{aligned} a' &= 7{\cdot}00 \text{ Å.U.} \\ b' &= 7{\cdot}44 \ ,, \\ c' &= 6{\cdot}56 \ ,, \end{aligned}\right\}.$$

The unit cell selected is the most nearly rectangular of all such possible minimum cells, and the space-group of course is C_i^1. The spacings calculated from the new unit cell are given in column 5 of Table III. and agree with all the measured spacings ; the new indices of each plane are given in column 6. These indices $(h'\,k'\,l')$ are obtained from the old indices as follows :

$$\left.\begin{aligned} h' &= h + l, \\ k' &= k + l, \\ l' &= 2l. \end{aligned}\right\}.$$

The occurring forms have rather simpler indices referred to the new cell, viz.: $\{100\}$, $\{010\}$, $\{1\bar{1}0\}$, $\{\bar{1}02\}$, $\{001\}$, $\{101\}$, $\{011\}$, $\{111\}$, $\{12\bar{1}\}$, $\{20\bar{1}\}$; the cleavages being parallel to $\{100\}$ and $\{10\bar{1}\}$. It is interesting to note that the planes giving strong X-ray reflexions have their indices considerably simplified in the new arrangement, whereas many of the planes having simple indices according to the original cell could not be found by means of X-rays.

It may be mentioned that Pasteur [*] originally measured some crystals presumed to be ammonium hydrogen fumarate crystals and found them to be monoclinic prismatic :

$$a : b : c = 1{\cdot}4303 : 1 : 0{\cdot}4299,$$

$$\beta = 93^\circ\, 9'.$$

These results show that the substance he investigated was either not ammonium hydrogen fumarate, or was a different crystalline modification altogether.

   * Pasteur, *Ann. chim. phys.* (3) xxxi. p. 91 (1851).

It will be seen from a comparison of the above examples that it is difficult to lay down any hard and fast rules for the determination of the true unit cell. Each case requires individual treatment, though a few general rules that may be useful have been published *. X-ray analyses similar to to the above, or the results of such analyses, will be found in many previous papers, since the determination of the true unit cell is the first of the many problems confronting the X-ray worker when he begins the examination of any crystalline substance.

My warmest thanks are due to Professor Sir W. H. Bragg for his continued interest in this research ; also to Mr. W. B. Saville, a fellow-worker at the Davy-Faraday Laboratory, who most kindly prepared for me the chemicals investigated. I have further to acknowledge my indebtedness to the Scientific and Research Department and to the Royal Institution for the financial and laboratory necessities supplied by them.

SUMMARY.

The limitations of the usual goniometric and of X-ray spectrometric measurements are discussed and compared. The following substances illustrate the comparison :—

A. *Potassium hydrogen chlormaleate.*—Rhombic bipyramidal. Axial ratio previously adopted,

$$a : b : c = 0.4841 : 1 : 0.3479.$$

X-ray measurements show that the c axis must be doubled, the true lengths of axes being

$$a = 7.62, \quad b = 15.74, \quad c = 10.95 \text{ Å.U.}$$

The true unit cell contains 8 asymmetric molecules, the Bravais lattice is Γ_o, and the space-group Q_h^{16}.

B. *Ammonium chlorfumarate.*—Previously stated to be monoclinic prismatic. X-ray measurements show that the class is probably monoclinic sphenoidal, lattice Γ_m, space-group C_2^2. There are 2 molecules, presumably asymmetric, per unit cell, for which

$$a = 9.30, \quad b = 6.70, \quad c = 6.73_5 \text{ Å.U.},$$
$$\beta = 108° 25'.$$

* R. W. G. Wyckoff, Amer. Journ. Sci. ix. p. 148 (1925).

C. *Ammonium hydrogen fumarate.*—Triclinic pinakoidal. Original crystallographic elements,

$$a : b : c = 0 \cdot 8587 : 1 : 0 \cdot 4558.$$

$$\alpha = 81^\circ \ 10\tfrac{1}{2}', \quad \beta = 89^\circ \ 59\tfrac{3}{4}', \quad \gamma = 75^\circ \ 17\tfrac{3}{4}'.$$

X-ray measurements show that the most nearly rectangular of possible minimum cells occupies twice the volume of the above and has dimensions,

$$a : b : c = 0 \cdot 9409 : 1 : 0 \cdot 8822.$$

$$\alpha = 107^\circ \ 1', \quad \beta = 117^\circ \ 58', \quad \gamma = 69^\circ \ 16'.$$

There are two asymmetric molecules per unit cell, corresponding to

$$a = 7 \cdot 00, \quad b = 7 \cdot 44, \quad c = 6 \cdot 56 \ \text{Å.U.}$$

The lattice is Γ_{tr}, space-group C_i^1.

XCV. *Distribution of Electrons in Atoms.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I SHALL be glad if you will allow me to direct attention to the fact that the distribution of electrons in atoms characterized by the sub-groupings 2 ; 2, 2, 4 ; 2, 2, 4, 4, 6 ; 2, 2, 4, 4, 6, 6, 8, did not originate with Mr. E. C. Stoner, as within recent months various papers published in your magazine have suggested. Mr. E. C. Stoner's paper suggesting this distribution of electrons appeared in your issue published on 1st October, 1924. This electronic distribution was with all relevant detail, however, originally proposed by me and was published six months earlier in the issue of 28th March, 1924, of the ' Review of Chemistry and Industry,' and reprinted with the chemical evidence proving the exact distribution of the electrons in every known element in terms of this scheme, and elaborated in detail in my book ' Chemistry and Atomic Structure,' published in October, 1924. I do not suggest that Mr. E. C. Stoner's work was not independent, but in view of the foregoing there can be no question of my priority in the matter of this electronic distribution in atoms. On the Continent and in America

my priority is acknowledged, but in my own country my work has failed even to be cited in papers in your magazine.

I am, Sir,
Yours faithfully,
J. D. MAIN SMITH.

Chemistry Dept.,
Birmingham University,
Edgbaston, Birmingham.
8 Sept. 1925.

XCVI. *A Note on the Photoactivation of Chlorine. By* EDMUND JOHN BOWEN, *M.A., Fellow of University College, Oxford* *.

A RECENT paper by W. Taylor on this subject (Phil. Mag. xlix. p. 1165, June 1925) seems likely to cause a serious misconception unless an error in the deductions is pointed out. The rate of combination of hydrogen and chlorine was measured in light of different wave-length ranges, and it was concluded that only the continuous part of the absorption band of chlorine was photo-effective. No account, however, was taken of the fact that the amount of light absorbed varies with the wave-length. For a weakly absorbing substance such as chlorine it is sufficient to assume that the amount of light absorbed is proportional to the extinction coefficient, and using the results of von Halban and Siedentopf (*Zeit. phys. Chem.* ciii. p. 71, 1922), we may correct Mr. Taylor's table as follows :—

Range of filter.	Reaction velocity.	Light absorbed. (Light intensity × mean absorption.)
4300–4800	100	100
4550–5000	27	30
4780–5370	14	13
5050–5570	0	0

It must be concluded, therefore, that the Ribaud fine-structure bands of chlorine are photo-active, and that the reaction rate is directly proportional to the number of light-quanta absorbed, within the limits of error.

A similar error appears in a paper by Coehn and Jung (*Zeit. phys. Chem.* cx. p. 722, 1924), where the amount of combination in hydrogen-chlorine mixtures in light of different wave-lengths is compared with the logarithm of the extinction coefficient, and the conclusion is drawn that there

* Communicated by the Author.

is a real photo-chemical threshold at 5400 Å., which, when converted into calories, is approximately equal to the heat of dissociation of chlorine. When the results are replotted with the extinction coefficient itself instead of its logarithm, it again appears that the rate of combination is closely proportional to the light absorbed ; and this is all that can be deduced from these experiments.

The question whether the heat of dissociation of chlorine is to be related to the absorption spectrum, an assumption made by several photo-chemists, is left undecided by these experiments.

In a paper presented to the Faraday Society (October 1925) it is shown that although the theory that free atoms play a part in photochemical processes is more useful in explaining a variety of phenomena than any other theory, attempts to equate directly absorption spectra energies to heats of dissociation or to " heats of activation " are unjustified practically and theoretically.

XCVII. *Notices respecting New Books.*

The Mechanical Investigations of Leonardo da Vinci. By IVOR B. HART, B.Sc., Ph.D. [Pp. vii + 240, with 7 plates and 136 figures.] (London : Chapman & Hall, 1925. Price 16*s*. net.)

LEONARDO DA VINCI was one of the great and most versatile men of the Middle Ages. His genius as sculptor and painter has been fully recognized, but his contributions to mechanical science, and in a lesser degree to mathematics, have not received the attention they deserve. This is doubtless due to the loss of his manuscripts to the world for over two hundred years, with the result that although many of his mechanical ideas were far in advance of those of his contemporaries, they had little influence in scientific development. It seems more than doubtful whether it was ever Leonardo's intention to publish the results of his labours : his manuscripts were written backwards, in nude characters, with his left hand, and are extremely difficult to decipher. Mr. Hart is of the opinion that he intended ultimately to reduce his notes to a form suitable for publication, but the evidence in favour of this view is very slender.

The volume under review contains a general account of mechanical science in the fifteenth century, and of the various sources which were available to Leonardo. His ideas on statics and dynamics, as evidenced by various passages in his notes, are summarized. His studies on the flights of birds and his design for a flying machine are then dealt with. Finally is given a

translation (the only English translation) of Leonardo's manuscript
" On the Flight of Birds."

The author has ably succeeded in showing to how great an
extent Leonardo's ideas were in advance of his time. To all who
are interested in the remarkably versatile genius of Leonardo da
Vinci this book will be full of interest. It is well printed and
illustrated with a large number of figures and diagrams from
Leonardo's original manuscripts.

An Introduction to Fluid Motion. By W. N. BOND, B.A., B.Sc.,
    D.Sc., A.R.C.S., F.Inst.P. [Pp. 94, with 38 figures.] (London :
    Edward Arnold & Co., 1925. Price 5s. net.)

THE author in his introduction remarks that the subject of fluid
motion " which has hitherto been studied as a branch of
mathematics—hydrodynamics—and as hydraulics, a branch of
engineering, has clearly reached the stage when it should be
recognized in its proper sphere, as an independent subject, forming
a branch of physics." Hydrodynamics is concerned mainly with
perfect fluids, incompressible and without viscosity. The problems
of fluid motion which are met with by the physicist are often not
capable of exact mathematical solution, but solutions must be
derived from general considerations supplemented by experiment.
For the most part, the required results cannot be found in existing
text-books.

The volume under review is intended to provide an introduction
and a guide to those embarking on the advanced study of fluid
motion. References to original publications are given. Extensive
mathematical knowledge is not required of the reader, and general
methods, such as the use of dimensions, are freely employed.
Some results are quoted without proof, whilst others are derived
by methods which, though not strictly rigorous, require only
elementary mathematics. A wide range of subjects is discussed
and illustrated by experimental work and results.

The author has carried out his task in an able manner, and the
book can be thoroughly recommended. Considering its size, the
price seems unnecessarily high.

The Principles of Thermodynamics. By GEORGE BIRTWISTLE,
    Fellow of Pembroke College, Cambridge. [Pp. ix + 163.]
    (Cambridge : At the University Press, 1925. Price 7s. 6d. net.)

THIS volume contains the substance of lectures given in the
University of Cambridge to men who may have been studying
mathematics, natural science or mechanical science. It does not
claim to be a complete text-book on the subject, and those portions
which demand a special knowledge of dynamical or physical theory,
such as the relation of statistical mechanics to thermodynamics,
the interpretation of entropy as probability, and the derivation of

Planck's law of radiation, are not discussed in detail. The volume does, however, give a careful and reasoned account of the foundations of the subject, of the two laws of thermodynamics, of Carnot's cycle, of entropy, and of the thermodynamic potentials. Numerous applications of these fundamental principles are discussed in illustration of the subject : these include the Rankine cycle, the porous plug experiment, the effect of pressure on boiling-points and melting-points, the phase rule and the general equilibrium of systems, osmotic pressure, thermoelectric phenomena, and radiation.

It will be realized that a very considerable field is covered, and that a very representative series of applications of thermodynamical principles is given. The treatment is straightforward ; the knowledge of mathematics required is very limited, and the exposition is, in general, clear, though there are exceptions, as *e. g.* § 36. The volume provides a convenient introduction to thermodynamical theory, and is a valuable addition to the not very extensive literature of the subject.

The Physics of the Developed Photographic Image. By F. E. Ross. [Pp. 217, with 82 figures.] (Rochester : Eastman Kodak Co., 1924. N. p.)

THIS volume forms No. 5 of the Monographs on the Theory of Photography from the Research Laboratory of the Eastman Kodak Co. It provides a valuable summary of present data on the behaviour and properties of photographic emulsions with theoretical interpretations of the facts wherever this is possible. So many variable factors require to be taken into consideration depending upon the instruments employed, the colour of the light used, the nature of the emulsion, and the treatment during and after development, that it is not surprising that, in many instances, results obtained by different investigators are discordant. Further research upon many of the topics dealt with is therefore desirable. There is also some danger in applying results obtained in the laboratory to astronomy, where the optical turbidity produced by the instrument may be far greater than that due to the film itself.

The complexity of the subject renders this summary the more valuable both to physicists and astronomers. Many of the properties of photographic emulsions which are considered are primarily of interest to astronomers, for whom an understanding of the laws of photographic action is essential for the correct interpretation of various results. The nature of the topics discussed can be judged from the chapter headings : The developed silver grain; Graininess; Astronomical photographical photometry; S arpness and resolving power; The mutual action of adjacent images; Film distortion and accuracy of photographic registration of position.

The book is illustrated with numerous excellent reproductions

of microphotographs of emulsion sections and with other figures. A good subject bibliography and indices of authors and subjects are added.

Scientific Papers, mainly on Electrodynamics and Natural Radiation. By the late S. B. McLaren, M.A., Professor of Mathematics in University College, Reading. [Pp. viii + 112, with portrait and 10 figures.] (Cambridge: At the University Press, 1925. Price 8s. 6d. net.)

The late S. B. McLaren was awarded an Adams Prize of the University of Cambridge in 1912 for an essay on the theory of radiation. At the time of his death from wounds at Abbeville on August 13, 1916, the final adaptation of his essay for publication was proceeding. The present volume, prepared by some of his personal friends, is intended to serve as a tribute to his memory and a memorial of his scientific activity. It contains a summary both of his published papers and of unpublished manuscripts, and embodies an account of the prize essay in so far as it has not been susperseded by others in the meantime. Sir Joseph Larmor has contributed the preface; Prof. Hugh Walker has written a personal appreciation. The obituary notice and an account of papers mainly on radiation and gravitation are by Dr. J. W. Nicholson. Papers and manuscripts on electromagnetic theory are edited by Prof. H. R. Hassé, whilst the manuscripts on the propogation of an arbitrary disturbance in a dispersive media are edited by Prof. T. H. Havelock.

McLaren was an original thinker, as is well shown in this volume. His early death was a great loss to British Science.

The Recent Development of Physical Science. By W. C. A. Whetham, M.A., F.R.S. Fifth, completely revised, edition. [Pp. xvi + 313, with 6 portraits and 42 figures.] (London: John Murray, 1924. Price 9s. net.)

Detailed reference to this well-known work is scarcely necessary. Published originally in 1904, the fourth edition appeared in 1909. The volume is familiar to all students of physical science, and is to be found in any good scientific library. During the fifteen years which have elapsed between the fourth edition and the present one, great advances have occurred in many of the subjects described, and there have been two new discoveries of fundamental importance—the quantum theory and the principle of relativity.

Whilst adhering, therefore, to his original plan, the author has found it necessary completely to revise the book, and to add much new matter dealing with the latest developments. The additions have been skilfully incorporated, and the volume remains a homogeneous whole, but has not been unduly enlarged. No more suitable volume can be recommended to the interested layman for providing an accurate, well-written account, in non-technical language, of the more important recent developments of physical science.

A Survey of Physics. By MAX PLANCK, Professor of Mathematics and Physics at the University of Berlin. Translated by R. JONES, M.A., and D. H. WILLIAMS, B.Sc. [Pp. vii + 184.] London: Methuen & Co., 1925. Price 6s. net.)

THE lectures delivered by Prof. Max Planck, translations of which are contained in this volume, deal with the following subjects :— The unity of the physical universe ; The place of modern physics in the mechanical view of nature ; New paths of physical knowledge ; Dynamical laws and statistical laws ; The principle of least action ; The relation between physical theories ; The nature of light ; The origin and development of the quantum theory.

They show in broad outline the directions in which many of the older ideas are being modified and the general trend of theoretical developments at the present time. This survey by one of the foremost and most progressive theoretical physicists of the present day will be found valuable by all students of science. The publishers are to be congratulated upon the addition of this volume to their lengthy series of translations of works by continental physicists.

The Elements of Mechanics. By F. S. CAREY, M.A., and J. PROUD-MAN, M.A., D.Sc. [Pp. ix + 311, with 234 figures.] (London : Longmans, Green & Co., 1925. Price 8s. 6d. net.)

THIS new text-book on Mechanics is intended to cover the advanced courses in schools and the first-year courses in universities. The authors, in writing it, have been guided by two main principles : Firstly, concepts and principles are introduced one at a time, so that any particular concept is not introduced until further progress without it is impossible ; in this way the logical structure of the subject is made clear to the student. Secondly, the authors have endeavoured to proceed from the concrete to the abstract, and from the more familiar to the less familiar. Thus the gravitational measure of force is introduced before the absolute measure and the concept of mass is discussed at a relatively late stage. Although this conforms to the practice in engineering instruction, its advantages to the reviewer appear doubtful.

Vector notation is introduced at an early stage, and statics and dynamics are developed side by side. Two chapters on elementary hydrostatics are included. An interesting chapter at the end deals with the rotation of the earth and celestial mechanics. A very elementary mathematical knowledge is required by the reader, and the calculus is not used. Collected at the end of the volume, in order not to break the continuity of the argument, is a large collection of examples on each chapter of the book for the student, some of which are worked in order to illustrate the general principles involved.

A Treatise on Electricity. By F. B. PIDDUCK. Second Edition. [Pp. xiv + 664, with 385 figures.] (Cambridge University Press, 1925. Price 21s. net.)

THE first edition of Pidduck's 'Electricity,' appeared in 1916, since which date there have been extensive advances in the subject. In the new edition these are fully dealt with, and the older matter has been revised where necessary so as to bring the volume thoroughly up to date. The new matter has been carefully incorporated so that the volume remains a homogeneous whole and is not—as too frequently is the case with second editions—a patchwork. The additions include accounts of modern work on Röntgen rays, on electric oscillations, on electricity in gases, and on atomic theory. The volume is written mainly for experimental physicists and senior students. It is not too much cumbered with mathematics, and it does not demand high mathematical attainments of its readers. The theory of practical methods and processes are given where necessary. For the science student requiring an accurate and up-to-date account of the subject no better volume is available: it can also be recommended to the mathematical student, to whom it will give a clear understanding of the physical meaning of the mathematical symbols which, to him, are too frequently symbols and nothing more.

Statics, including Hydrostatics and the Elements of the Theory of Elasticity. By H. LAMB, M.A., LL.D., Sc.D., F.R.S. Second Edition. [Pp. xii + 357, with 181 figures.] (Cambridge University Press, 1924. Price 12s. 6d. net.)

THE second edition of this well-known volume differs from the first edition mainly by several additions to the chapters on Elasticity and the insertion of some additional examples. It still remains one of the best text-books for mathematical students of tripos standard, who have an elementary knowledge of the calculus. The inclusion in one volume of statics, hydrostatics including the laws of gases, capillarity and the theory of elasticity, so that the essential unity of these several branches of the subject is brought home to the student, has much to recommend it. Prof. Lamb is well known as an excellent and successful teacher, and this is shown by the care which is taken to explain points which are found difficult of comprehension by the average student. An important feature of the work is the prominence given to graphical statics and other geometrical methods; such methods are valuable because the absence of mathematics enables the physical aspect of the subject to be made more evident. The extensive series of examples, carefully selected as illustrating statical principles rather than as mathematical exercises, will be found of great value both to teacher and student.

XCVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

February 4th, 1925.—Dr. J. W. Evans, C.B., F.R.S.,
President, in the Chair.

THE following communication was read :—

' The Petrology of the District between Nevin and Clynnog-fawr (Carnarvonshire).' By Albert Heard, M.Sc., Ph.D., F.G.S.

The area described occupies about 30 square miles of the northern portion of the Lleyn peninsula, and is situate between the small towns of Nevin and Clynnog-fawr.

Drift obscures most of the valleys, and conceals the greater part of the areas underlain by unaltered shales.

Most of the sedimentary rocks consist of dark purplish-grey shales of *Didymograptus-bifidus* age, together with their metamorphosed representatives.

In the north-western part of the area unfossiliferous pale-grey shales are present. These shales contain numerous ashy and fine-grained gritty bands, and occur immediately above the *D.-bifidus* Beds,

The pisolitic iron-ores of Trwyn-y-Tal, which appear to occupy the same stratigraphical horizon as the pale-grey shales, are described. These ores are greatly deformed mechanically. Their possible origin by bacterial agency is discussed.

A large proportion of the exposed rocks consists of an igneous complex of post-Lower Arenig—pre-Old Red Sandstone age.

The intrusive rocks present many petrological variations, including numerous different types of granite and quartz-porphyries, granophyres, porphyries of intermediate composition, and basic rocks.

Andesites, with spilitic affinities, occur in the south-eastern portion of the district. They are interbedded with sedimentary rocks, and have a flow-breccia at the base.

Nodular rhyolites, with much included jasper, occur in the north of the area, and are characterized by large felspar-phenocrysts. They are petrologically unlike any known Ordovician lavas. These porphyritic rhyolites appear to underlie the *Didymograptus-bifidus* Beds, but the strata upon which they rest are not exposed. Their age is a matter of conjecture ; it is concluded that they represent either Pre-Cambrian extrusives, or Arenig lavas poured over a Pre-Cambrian floor.

The invaded sedimentary rocks exhibit almost every stage of thermal metamorphism: the greatest degree of alteration has resulted in the formation of a fine-grained garnet-sericite-schist.

One of the most interesting of the many petrogenetical problems which have arisen during the investigation is associated with the peculiar 'banding' of the constituents of the coarser-grained intrusive masses. Several excellent exposures of the junctions of these bands reveal the fact that neither hybridism nor any apparent chilling is exhibited at the junction of adjacent 'bands'. Moreover, the uppermost band invariably consists of the most basic rock.

February 20th.—Dr. J. W. Evans, C.B.E., F.R.S.,
President, in the Chair.

The PRESIDENT delivered his Anniversary Address, dealing with the subject of regions of tension, evidenced by joints, slip-faults, and dykes. He enumerated the different causes of local tension, including torsion, but pointed out that, although the latter was found by Daubrée to give systems of fractures at right angles to one another, these might also be produced in any area with maximum and minimum directions of tension. He showed that Western Europe was largely characterized by tension towards the south-west, but the north-westward tension prevailed in North-Western Ireland and North-Western Scotland. The south-westward tension appeared to represent a slow drift towards the Atlantic 'deep' in the Bay of Biscay running north-westwards from Cape Breton, and the north-westward tension seemed to represent a drift towards the 'deep' trending north-eastwards between Rockall and Ireland. These 'deeps' themselves were to be attributed, not to 'foundering' but to a drift of the 'sial' masses of the Central Atlantic banks to the south-west and north-west respectively.

The nature and origin of the igneous rocks associated with tension were discussed. Other regions of tension were then described, especially that of Eastern Africa. Finally, the theories that have been advanced as to the cause of the drift of continental masses were considered.

February 25th.—Dr. J. W. Evans, C.B.E., F.R.S.,
President, in the Chair.

The following communication was read :—

'The Geology of Cader Idris (Merionethshire).' By Prof. Arthur Hubert Cox, D.Sc., Ph.D., F.G.S.

Cader Idris is an escarpment of Ordovician igneous rocks south of the Harlech Dome. An account of previous research is given.

The strata have a general southward or south-eastward dip of about 40°, and the succession is as follows :—

Thickness in feet

CARADOCIAN.	Talyllyn Mudstones	Grey-blue banded mudstones, with *Amplexograptus arctus* in the lowest beds	4000
LLANDEILO.	Upper Acid Group	Rhyolitic and acid andesitic ashes and lavas	900–1500
	Llyn Cau Mudstones		500
	Upper Basic Group	Pillow-lavas (spilites), with tuff and chert-bands	400– 500
	Llyn-y-Gader Mudstones and Ashes	Grey-blue mudstones, with adinoles and massive ashes—*Glyptograptus teretiusculus*	450– 600
	Oolitic iron-ore		10– 20
	Lower Basic Group	Pillowy spilitic lavas, with many ash- and shale-bands	1500
LOWER LLANVIRN.	Cefn Hir Ashes	Massive agglomeratic ashes	500
	Bifidus Shales and Grits	*Didymograptus bifidus,* etc.	300– 600
ARENIG.	Lower Acid Group	Rhyolite-lavas and ashes	500–1000
	Basement-Beds	Striped arenaceous flags and grits..................	150– 200

Unconformity
UPPER CAMBRIAN.

The volcanic rocks thus have a much greater time-range than had been proved hitherto. The four volcanic groups are separated one from the other by sediments of thicknesses so considerable that each represents a distinct episode.

Intrusive rocks are represented by numerous dolerite-sills, and by two great sills of granophyre, which are later than the dolerites. No basic intrusions occur above the highest basic extrusive rocks, and no acid intrusions above the highest acid extrusives. The granophyres seem to be related petrologically to the invaded rhyolites, and their intrusion is assigned to a pre-Bala or early Bala period.

The main structures have a north-east to south-west trend; but there is also a regular system of north-and-south minor folds that often cause a marked deflexion of outcrops. This minor folding was operative in pre-Ordovician times, as shown by the relation of the Ordovician rocks to the Cambrian; also during Ordovician time, for the folds seem to have influenced sedimentation, and they controlled the emission and extension of the major intrusions, which originated in anticlines and terminated in synclines; the folds were further active in post-Silurian times.